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CONDUCTIVITY AND CATAPHORETIC SPEED MEASUREMENTS OF BENZOPURPURIN 4B, CONGO RED AND SKY BLUE F.F.

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Received July 23, 1936.

Although the dyeing of cotton by direct dye-stuffs has been practised for a long time, their action on the fibres has not been clearly understood. The substantive dye-stuffs have very high molecular weights and in aqueous solutions, they exist in the form of colloidal electrolytes.[1] In view of the colloidal chemical nature of the solutions of the direct dyes and the necessity of the presence of salts while dyeing, many investigators have studied their coagulation by and diffusion in the presence of different electrolytes. Benzopurpurin 4B, Congo Red and Sky Blue F.F. have already been the subject of numerous physico-chemical investigations and it was therefore decided to determine their conductivity and cataphoretic speed to see if these particular results can throw any light on the mechanism of dyeing by the substantive dye-stuffs.

Experimental.

It is a well-known fact that the technical dye-stuffs contain electrolytic and organic impurities, and for any investigational work, it is of fundamental importance to use the dyes in their purest form. Their purification is however not very simple as they are of complex nature and may contain their isomerides and homologues which are difficult to remove. Many methods which have been used for purification are open to objection as the dye is produced in a different state. The method adopted by Robinson and coworkers[2] was used for the precipitation of the dyes employed in this investigation as it is free from objections. The relative viscosity at 30° C. and the pH of solutions of the dyes so purified were as given below :—

Dye	Concentration	Relative Viscosity	pH
Benzopurpurin 4B ..	0·5%	1·039	7·10
Congo Red ..	0·4%	1·096	7·18
Sky Blue F.F. ..	0·4%	1·044	7·00

Conductivity water was used for preparing all the solutions.

The conductivity was measured by the usual method using an amplifying circuit similar to the one used by Lorenz and Klauer,[3] the details of the method being the same as those given by Desai and co-workers.[4]

The cataphoretic speed was measured in the same way as done by Desai and Borkar.[5] The upper liquid in these measurements consisted of a solution of sodium chloride having the same conductivity as the dye solution.

Benzopurpurin 4B was also subjected to dialysis in parchment paper bags and its cataphoretic speed measured at different stages of dialysis.

All the measurements of conductivity and cataphoretic speed were carried out in an air thermostat at a temperature of 30° C.

Results.

The results of these experiments are given in the tables below. The cataphoretic speed readings have been corrected for viscosity by taking the viscosity of water as unity. The concentration of the electrolyte is expressed in mols per litre of the mixture.

TABLE I. *Benzopurpurin 4B.*

Dye Conc. %	Cataphoretic speed × 10^5						
	Period of dialysis						
	0	4 days	8 days	12 days	16 days	20 days	24 days
0·025	17·54	30·50	28·32	25·20	17·01	16·45	15·89
0·05	19·62	33·61	30.19	27·18	18·12	17·51	16·91
0·10	26·39	36·63	33·21	27·78	27·18	27·00	26·15
0·20	32·57	39·25	39·66	30·80	28·01	27·78	26·70
0·30	38·04	42·33	44·39	36·54	32·24	29·68	27·18

TABLE II. *Benzopurpurin 4B.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed × 10^5
0·1795	125·65	17·54
0·3592	107·75	19·62
0·7184	99·30	26·39
1·4368	92·75	32·57
2·1552	85·05	38·04

TABLE III. *Benzopurpurin 4B.*
(Conc. 0·7184 N).

Conc. of NaCl	Cat. speed × 10^5
0·000	26·39
0·684	33·81
1·368	30·19
2·052	22·64
2·736	21·74

TABLE IV. *Congo Red.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed × 10^5
0·3453	116·20	22·64
0·6906	102·90	23·54
1·3812	97·30	36·23
2·0718	90·65	40·76
2·7624	90·15	45·50

TABLE V. *Congo Red.*
(Conc. 0·6906 N).

Conc. of NaCl	Cat. speed × 10^5
0·000	23·54
0·342	25·60
0·684	27·50
1·368	36·23
2·052	30·53
2·736	23·54

TABLE VI. *Sky Blue F.F.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed × 10^5
0·063	342·5	17·21
0·126	342·0	18·57
0·252	342·3	27·09
0·504	342·3	33·06
0·756	342·3	36·69
1·008	280·3	..

TABLE VII. *Sky Blue F.F.*
(Conc. 0·252 N).

Conc. of $BaCl_2$	Cat. speed × 10^5
0·0	27·09
0·2	31·57
0·4	41·93
0·6	31·73
0·8	14·49

Discussion.

(*a*) *Changes in cataphoretic speed during dialysis.*—It will appear from Table I that with the progress of dialysis (horizontal rows) the cataphoretic speed first increases and then decreases in all the cases. It will also be noticed that there is a tendency for the cataphoretic speed to remain constant when the dye solution is subjected to dialysis for long periods. The changes in the cataphoretic speed with the progress of dialysis are similar to those observed by Desai and co-workers in the case of colloidal gold,[6] ferric hydroxide,[5] thorium hydroxide[7] and Prussian blue.[8]

As stated before, the pH of the pure Benzopurpurin 4B dye solution was 7·1; the dye therefore does not hydrolyse in aqueous solution. Matters, however, become different when the solution of the dye is dialysed against pure water. As a result of the influence of the parchment membrane the dye will hydrolyse[9] and some NaOH pass out in the dialysate. The solution in the parchment bag will contain the undissociated dye [if the dye (salt) is not completely dissociated], the dye ions, Na-ions and H-ions.

For spherical particles obeying Stokes' law the following equation holds good :—

$$U_0 = \frac{E}{6\pi\eta r}$$

where U_0 = Cataphoretic speed under unit potential gradient.

E = Total charge on the particle.

r = Radius of the particle.

and η = Viscosity.

The total charge being proportional to the total surface area, *i.e.*, the square of the radius, the cataphoretic speed would be greater for the larger particles assuming that the shape of the particles does not change materially during aggregation and the frictional resistance does not increase with aggregation at the same rate as the total surface charge. The initial increase in the cataphoretic speed with the progress of dialysis is therefore due to the formation of large ionic micelles. The turbidity of the dye solution was found to increase during dialysis thus showing that aggregation of the dye ions to form ionic micelles had taken place.

In view of the increase of turbidity (*i.e.*, of the size of the ionic micelles) of the dye solution with the progress of dialysis, the cataphoretic speed should have continuously increased instead of only upto a certain stage of dialysis. The subsequent decrease of cataphoretic speed may probably be due to the following causes :—

(1) The increase in the hydration of the ionic micelles during dialysis will decrease the cataphoretic speed to a certain extent.

(2) The ' inclusion effect,'[10] *i.e.*, the inclusion of the gegenions (oppositely charged ions) will increase on standing during dialysis and the cataphoretic speed will decrease. This inclusion effect can be taken to mean preferential adsorption of the oppositely charged ions (gegenions).

It is considered that the influence of the second factor is mainly responsible for the subsequent decrease of the cataphoretic speed.

In the early stages of dialysis the inclusion effect will also be there but the cataphoretic speed increases because the effect of aggregation is more pronounced than that of inclusion.

The tendency for the cataphoretic speed to remain constant on dialysing the solution for long periods is probably due to effect of aggregation and inclusion being about the same.

It may be mentioned that the explanation which Desai and collaborators[5,6,7,8] have advanced for the ∩-shaped cataphoretic speed-dialysis curves for the hydrophobic sols cannot be utilised in the present instance because in the former case the charge on the particles is due to preferential adsorption of the ions of the peptising electrolyte whose amount continuously decreases during dialysis, while in the latter case the dye ion itself represents the micelle ion.

(*b*) *Changes in conductivity and cataphoretic speed with dilution.*—It will appear from Tables II and IV that in the case of Benzopurpurin 4B and Congo Red the equivalent conductivity continuously decreases, while the cataphoretic speed continuously increases on increasing the concentration of the dye solution. In the case of Sky Blue F.F. (Table VI) on increasing the concentration of the dye solution the equivalent conductivity remains more or less constant at first and decreases later while the cataphoretic speed continuously increases as in the case of the other dyes.

In his extensive researches on soap solution McBain[11] observed a remarkable increase of equivalent conductivity with increasing concentration in the aqueous solutions of soaps at about N/10 and higher concentrations. He ascribed the increase in equivalent conductivity to the aggregation of ions of one kind to form ionic micelles. As discussed by Moilliet, Collie, Robinson and Hartley[10] if ' m ' ions aggregate to form ionic micelles, their velocity will be multiplied by $m^{\frac{2}{3}}$ and as they carry the same amount of electricity as before their contribution to the conductivity will be multiplied by the same amount. The above arguments however apply only in the case of very dilute solutions in which the ' inclusion effect ' of Robinson and

others and the ' atmosphere effect ' of Debye, Hückel-Onsager theory are both negligible. It is likely that even in most dilute dye solutions multivalent ionic micelles will be there and the ' inclusion effect ' and the ' atmosphere effect ' will be very large as compared with the ordinary electrolytes. Thus the increase in conductivity due to Stokes' law effect of aggregation—termed primary effect—will be levelled out by the inclusion and atmosphere effects —termed secondary effects—which will decrease the conductivity. The decrease of conductivity due to the secondary effects will increase with the increase in the number of ions aggregating to one micelle, *i.e.*, with concentration. The dye solutions tried here are generally moderately concentrated and the conductivity has decreased with increase in concentration probably due to the fact that the secondary effects are more pronounced than the primary effect. In the case of Sky Blue F.F. the conductivity has remained constant between concentrations 0·063 N and 0·756 N ; this is probably due to the fact that the primary effect and the secondary effects balance each other. For the same equivalent concentration the conductivity of Sky Blue F.F. is greater than that of either Benzopurpurin 4B or Congo Red ; this perhaps indicates relatively high mobility of the dye ion in the case of Sky Blue F.F.

From Tables II, IV and VI it will appear that the cataphoretic speed has increased with concentration for all the three dye solutions. In view of the arguments discussed in section (*a*) the increase in the cataphoretic speed is due to aggregation of the dye ions to form ionic micelles. The cataphoretic speed results thus show that the size of the particles increases with concentration for Benzopurpurin 4B, Congo Red and Sky Blue F.F.

The next question to be considered is why the conductivity results do not give evidence of aggregation although the cataphoretic speed results definitely indicate formation of large micelles. Moilliet, Collie, Robinson and Hartley[10] have discussed the difficulties of obtaining information regarding aggregation from conductivity measurements as a result of secondary effects mentioned above. They have also pointed out that the secondary effects might be less marked if mobilities or transport numbers of the ionic micelles are determined instead of conductance. They have shown that the atmosphere effect will decrease both mobility and transport number as conductance ; the inclusion effect though tending to decrease the mobility slightly and conductance greatly will actually increase the transport number quite markedly. The transport number will not however increase due to aggregation to the same extent as mobility and conductance. Robinson[12] observed that the mobility of *meta*-Benzopurpurin increases with increase in concentration in dilute solutions although the conductivity measurements

under the same conditions did not give evidence of aggregation. He also found that the mobility of Benzopurpurin 4B decreases with increase in concentration from 0·004 N to 0·01 N. Moilliet, Collie, Robinson and Hartley[10] however determined transport numbers of the 4B dye and found evidence of aggregation with increase in concentration from about 0·001 N to 0·012 N. From the present results (Table II) it will appear that the cataphoretic speed gives evidence of aggregation with increase in concentration from 0·1795 N to 2·1552 N. The cataphoretic speed determinations would thus appear to be more important than the transport number measurements for getting an idea about aggregation of ionic micelles.

The fact that ionic micelles aggregate on increasing the concentration of the 4B dye is further supported from stability determinations. It is found that the flocculation value with NaCl decreases as the concentration of the dye is increased. If aggregation of ionic micelles had not taken place, the amount of NaCl required to produce a given degree of turbidity in a certain time would be greater for a concentrated than for a dilute solution.

(*c*) *Changes in cataphoretic speed in the presence of salts.*—It will appear from Tables III, V and VII that on adding small increasing amounts of salts to the dye solutions the cataphoretic speed increases in the beginning but decreases later. Robinson and Moilliet[13] also found an increase in the cataphoretic speed of the particles of Benzopurpurin 4B on the addition of electrolytes.

The initial increase in the cataphoretic speed on the addition of salt can be due to (i) preferential adsorption of the similarly charged ions and (ii) aggregation of the ionic micelles. It is considered that the increase in the cataphoretic speed is mainly due to the second factor. The increase in the turbidity of the dye solution on the addition of salt would also support aggregation of the particles. It is likely that some oppositely charged ions might also be preferentially adsorbed but the decrease in the cataphoretic speed on account of this is not perceptible owing to the marked effect of aggregation.

As the dye solution actually coagulates (increase in the size of the particles) on the addition of large amounts of salt one would expect an increase in the cataphoretic speed throughout. It will however appear that the cataphoretic speed has actually decreased on adding relatively large amounts of salts. This is probably due to the marked preferential adsorption of the gegenions which does not allow the effect of aggregation to be noticed at all.

These results are similar to those obtained by Valkó[14] who determined the diffusion coefficients by the porous plate method of the 4B dye, Congo

Red and Chicago Blue 6B (identical with the Sky Blue F.F.) in the presence of different small amounts of NaCl and found that the particles aggregate in all the cases.

(*d*) *Bearing of the present results on the mechanism of dyeing by direct dye-stuffs.*—A very interesting and important discussion on the various theories on dyeing by direct dye-stuffs took place at London in September 1934 under the auspices of the Faraday Society, and it is proposed to examine some of the views expressed there in the light of the present results and conclusions. Morton[15] has stated that in the presence of small amounts of NaCl the degree of dispersion of pure dye increases although on adding relatively large amounts of salt the degree of dispersion decreases. Our results do not support the view that the degree of dispersion of the dye particles increases in the presence of salt. The results of diffusion experiment of Valkó[14] also show that the degree of dispersion of the ionic micelles does not increase on raising the salt concentration.

Neale and others[16] have measured the adsorption of the dye-stuffs by fibres and observed that it increases with increase of salt concentration at least upto a certain concentration. They have calculated the rate of diffusion by the application of Hill's[17] equation and found that the rate of diffusion first increases, reaches a maximum and then decreases. Their diffusion coefficients so calculated do not therefore agree with the results of Valkó.[14] according to whom the diffusion coefficients continuously decrease on adding increasing amounts of salt. It must however be stated that the adsorption results of Neale and co-workers[16] can be easily understood even on the basis of continuous increase in the size of the dye ions on the addition of increasing amounts of salt. Greater adsorption of the dye with the increase in salt concentration might probably take place in spite of a decrease in the diffusion coefficient, because relatively larger ionic micelles will be adsorbed instead of smaller ones (with little or no salt) as long as the ionic micelles are not bigger than the capillary pores of the cellulose. Once the micelles become of the same size as or larger than the capillary pores, further aggregation will not increase adsorption. Thus there will be an optimum concentration of salt for dyeing at which maximum dye can be adsorbed ; smaller or larger amounts of salts than the optimum will mean less adsorption of the dye. The experience of the practical dyer that too much of the salt causes a waste of dye is to be explained on the basis that some of the ionic micelles reach such a large size that they cannot be adsorbed by the fibre.

Robinson[18] has suggested that the effect of the negative charge in the viscose capillaries, which will oppose the passage of the dye whose ionic micelles are also negatively charged, will be almost completely suppressed

by the presence of the salt and hence the dye will be allowed to pass freely. According to him the effect of salt on the degree of dispersion of the dye is only of secondary importance. It may however be stated that increased adsorption of the dye in the presence of salt can easily be explained, as pointed out above, on the basis of aggregation and that it is not necessary to consider the effect of charge on the viscose capillaries on the adsorption of the dye whose micelles are also negatively charged.

Neale[19] has also stated that it is difficult to be dogmatic with regard to the importance of aggregation in dyeing with direct cotton colours. His view is that there is only slight aggregation and that at the elevated temperatures (usually 90° C.) used in his experiments aggregation of the dye is of little or no importance except at exceptionally high concentrations of the added salts. We would like to mention that although there will be considerably less aggregation of the dye at 90° C. than at ordinary temperatures, it has been shown by Morton[15] that the direct dyes are dissolved colloidally to some extent even at 75° C. In view of this it is highly probable that even at the " boil " the addition of small amounts of salts would produce appreciable aggregation of dye micelles, although certainly less than at ordinary temperatures.

It is now possible to explain in a simple manner the process of dyeing by substantive dye-stuffs in the presence of salts on the basis of aggregation of dye ions. If salt is not added to the bath, the size of the dye ions may be so small (amicronic size or even smaller) that they may come out from the fibre on washing, *i.e.*, the colour will not be fast to wash. If two much of salt is added, the size of the ionic micelles will become very large and only a small amount of the dye will be adsorbed, some dye actually remaining in the bath as stated before. The advantage of dyeing at higher temperatures instead of at ordinary temperatures is that as a result of the swelling of the fibre relatively large sized dye micelles are adsorbed in the presence of salt in the former case and when the ordinary temperature is attained the dye becomes so fixed in the fibre due to shrinking of the latter that it cannot be washed out easily (colour fast to washing). If salt is not present in the dye bath only small sized micelles will be adsorbed at relatively high temperatures as the degree of dispersion of the dye increases with temperature and the fastness to washing will be less unless a very large amount of the dye is added to increase the size of the micelles adsorbed, but a considerable amount of dye will be wasted in that case. Dyeing at ordinary temperatures even if salt is present in the bath will also not give desired fastness as the micelles adsorbed will be easily washed out due to absence of shrinking of the fibre.

Summary and Conclusions.

Measurements of conductivity and cataphoretic speed of pure Benzopurpurin 4B, Congo Red and Sky Blue F.F. have been made and it is found that on increasing the concentration of the dye solutions although the equivalent conductivity continuously decreases the cataphoretic speed increases regularly. The cataphoretic speed of Benzopurpurin 4B first increases and then decreases with the progress of dialysis. On adding small increasing amounts of sodium chloride to Benzopurpurin 4B and Congo Red and barium chloride to Sky Blue F.F. the cataphoretic speed first increases and then decreases. The changes in conductivity and cataphoretic speed are explained on the basis of aggregation of the dye ions to form ionic micelles. It is shown that the process of dyeing of cotton fibre by substantive dyestuffs in the presence of salt can be easily understood on the basis of aggregation of dye ions.

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LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part II. Elasticity-Constants of Aragonite.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

In a preceding paper,[1] referred to hereafter as I, the lattice energy of the crystals of Aragonite and the value of n, the index of the repulsive forces were calculated. In this paper we proceed with the calculations of the elasticity-constants. In the case of such elasticity-constants, as depend on the ionic deformations, no agreement between the experimental values and the values calculated on simple theories can be expected. We restrict ourselves to the calculation of only those constants which do not essentially depend on the ionic deformation.

The method depends in being able to find out systems of parallel neutral planes in the crystal. We assume a deformation by which the distance between the consecutive planes is uniformly changed. Though the longitudinal stress in the crystal is always connected with a transversal contraction, we neglect the changes in the distances of the ions inside each plane. This amounts to assuming that the contraction has no great influence on the value of the elasticity-constants in the longitudinal direction. The results of the calculations will amply justify this procedure.

The elasticity-constant c_{jh} consists of two parts c^e_{jh} and c^r_{jh}, which are due to the electro-static and the repulsive forces, respectively. These two parts will be calculated separately.

§1. *Systems of Parallel Neutral Planes.*

Fig. 1 gives the projection of the crystal on the xy plane. Planes which are perpendicular to the x-axis are all neutral planes ; so also the planes perpendicular to the line in the x-y plane making an angle $\tan^{-1} b/3a$ with the y-axis, are all neutral. We denote this angle by θ, so that $\tan\theta = b/3a$ .. (1, 1)

[1] B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1.

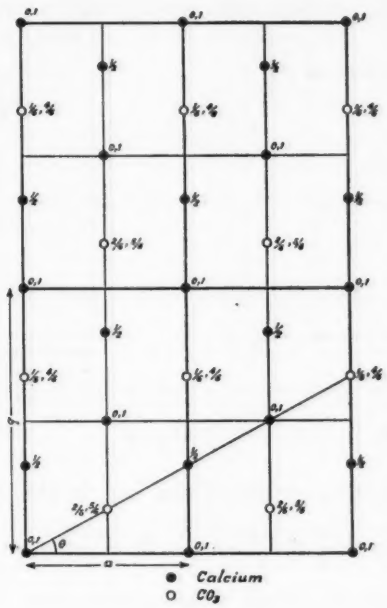

FIG. 1.

The numbers in the figure denote the ' heights ' as multiples of c above the plane $z = 0$.

In the system of parallel neutral planes perpendicular to the x-axis the distance d, between consecutive planes, is given by

$$d = a/2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 2)$$

Fig. 2 shows the arrangement of the ions in the planes at $x = 0$, $\pm a$, $\pm 2a$, ... $\pm na$, ...

The cell of the plane-lattice consists of 4 ions whose y and z co-ordinates are given by

$$\left.\begin{array}{lll} k = 1, \text{ Calcium ion} & (0, \ 0) \\ k = 2, \text{ Calcium } ,, & \left(\frac{b}{3}, \frac{c}{2}\right) \\ k = 3, \ CO_3 \quad ,, & \left(\frac{2b}{3}, \frac{c}{6}\right) \\ k = 4, \ CO_3 \quad ,, & \left(\frac{2b}{3}, \frac{2c}{3}\right) \end{array}\right\} \quad .. \quad .. \quad .. \quad (1, 3)$$

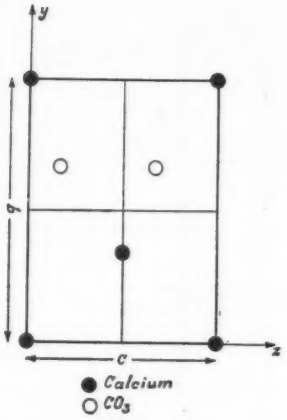

FIG. 2.

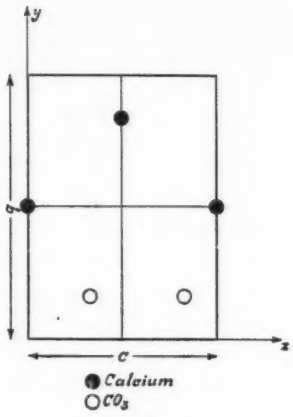

FIG. 3.

Fig. 3 shows the arrangement of the ions in the planes at

$$x = \pm \frac{a}{2}, \pm \frac{3a}{2}, \ldots\ldots, \pm \frac{2n+1}{2} a, \ldots\ldots$$

The y and z co-ordinates of the 4 ions constituting a cell of the plane-lattice are given by

$$\left.\begin{array}{lll} k = 1, \text{ Calcium ion} & \left(\frac{b}{2}, 0\right) \\ k = 2, \text{ Calcium } ,, & \left(\frac{5b}{2}, \frac{c}{2}\right) \\ k = 3, \text{ } CO_3 \quad ,, & \left(\frac{b}{6}, \frac{c}{3}\right) \\ k = 4, \text{ } CO_3 \quad ,, & \left(\frac{b}{6}, \frac{5c}{6}\right) \end{array}\right\} \quad \ldots \quad \ldots \quad \ldots \quad (1, 4)$$

In the other system of parallel neutral planes the distance between consecutive planes is given by

$$d_\theta = \frac{ab}{\sqrt{9a^2 + b^2}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1, 5)$$

For the representation of this system we choose a system of co-ordinates x_θ, y_θ, z_θ such that the z_θ-axis coincides with the z-axis and Oy_θ is perpendicular to the planes. Fig. 4 shows the arrangement of the ions in the plane $y_\theta = 0$. All planes belonging to this system have exactly similar ionic

arrangements ; the consecutive planes are displaced along the Ox_θ-axis through a distance a_θ given by

$$a_\theta = 3\,\frac{a^2}{\sqrt{9a^2+b^2}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 6)$$

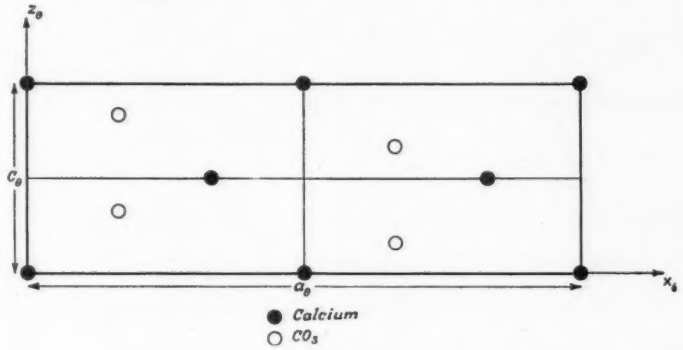

FIG. 4.

The dimensions of the unit cell of the plane-lattice are given by

$$\left.\begin{aligned} a_\theta &= \sqrt{9a^2+b^2} \\ \text{and} \quad c_\theta &= c \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 7)$$

The cell consists of 8 ions, the x_θ and z_θ co-ordinates of which are given by :

$$\left.\begin{aligned} &k = 1, \text{ Calcium ion } (0, \quad 0) ; \quad k = 5, CO_3 \text{ ion } \left(\frac{a_\theta}{6}, \quad \frac{c}{3}\right) \\ &k = 2, \text{ Calcium } ,, \left(\frac{a_\theta}{3}, \frac{c}{2}\right); \quad k = 6, CO_3 ,, \left(\frac{a_\theta}{6}, \frac{5c}{6}\right) \\ &k = 3, \text{ Calcium } ,, \left(\frac{a_\theta}{2}, \quad 0\right); \quad k = 7, CO_3 ,, \left(\frac{2a_\theta}{3}, \frac{c}{6}\right) \\ &k = 4, \text{ Calcium } ,, \left(\frac{5a_\theta}{6}, \frac{c}{2}\right); \quad k = 8, CO_3 ,, \left(\frac{2a_\theta}{3}, \frac{2c}{3}\right) \end{aligned}\right\} \quad .. \quad (1, 8)$$

Denoting the elasticity constants in the directions perpendicular to the planes of these two systems by c_{11} and c_{22}^θ respectively we have

$$\left.\begin{aligned} c_{11} &= c_{11}^e + c_{11}^r \\ \text{and} \quad c_{22}^\theta &= c_{22}^{e\theta} + c_{22}^{r\theta} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 9)$$

§2. *Evaluation of* c_{11}^e *and* $c_{22}^{e\theta}$.

We take any one of the first system of planes, say the plane $x = a/2$ and calculate the potential per unit area of this plane due to all planes on one

side of this plane, say the negative side of the x-axis. Let ϕ_j (1), ϕ_j (2), ϕ_j (3) and ϕ_j (4) denote the potential at the 4 lattice points of a unit cell of the plane $x = a/2$ due to the jth adjoining plane. The potential per unit area of the plane $x = a/2$ due to the jth adjoining plane is given by

$$\Phi_j = \frac{\phi_j(1) + \phi_j(2) + \phi_j(3) + \phi_j(4)}{bc} \quad .. \quad .. \quad .. \quad (2, 1)$$

Φ, the potential per unit area due to all planes, on one side, is

$$\Phi = \sum_{j=1}^{\infty} \Phi_j \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 2)$$

The electro-static part of the elasticity-constant is given by

$$c_{11}^e = \frac{a}{2bc}\left[\frac{\partial^2 \Phi_1}{\partial x^2}\right]_{x=\frac{a}{2}} + \frac{a}{bc}\left[\frac{\partial^2 \Phi_2}{\partial x^2}\right]_{x=a} + \frac{3a}{2bc}\left[\frac{\partial^2 \Phi_3}{\partial x^2}\right]_{x=\frac{3a}{2}} + \cdots \quad .. \quad (2, 3)$$

We have[2]

$$\phi_1(x, y, z) = \frac{2\pi}{bc}\, 2e \sum_{l,m}{}' e_{x,y,z} \frac{e^{-\alpha_{l,m}|x|}}{\alpha_{l,m}} e^{2\pi i (l\, y/b + m\, z/c)} f_1(l, m) \quad .. \quad (2, 4)$$

where $\alpha_{l,m} = 2\pi \left| \frac{l}{b} + \frac{m}{c} \right|$ .. .. (2, 5)

and $f_1(l, m) = (\cos 0 - i \sin 0) + \left[\cos\left(\frac{2\pi l}{3} + m\pi\right) - i \sin\left(\frac{2\pi l}{3} + m\pi\right)\right]$

$$- \left[\cos\left(\frac{4\pi l}{3} + \frac{m\pi}{3}\right) - i \sin\left(\frac{4\pi l}{3} + \frac{m\pi}{3}\right)\right]$$

$$- \left[\cos\left(\frac{4\pi l}{3} + \frac{4m\pi}{3}\right) - i \sin\left(\frac{4l\pi}{3} + \frac{4m\pi}{3}\right)\right] \quad .. \quad (2, 6)$$

$e_{x,y,z}$ is the electric charge at the point (x, y, z).

Substituting the co-ordinates from (1, 4)

$$\phi_1(k) = \frac{2\pi}{bc}(2e)^2 \sum_{l,m}{}' \frac{e^{-\alpha_{l,m}|x|}}{\alpha_{l,m}} \mathrm{F}_1^{l,m}(k) \quad .. \quad .. \quad .. \quad (2, 7)$$

The function $\mathrm{F}_j^{l,m}(k)$ is given by

$$\mathrm{F}_j^{l,m}(k) = f_j(l, m) \times g_{l,m}(k) \quad .. \quad .. \quad .. \quad .. \quad (2, 8)$$

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[2] M. Born, *Ency. der Math. Wiss.*, **3**: *Physik.*, §37, p. 722, eqn. 413.

The g's are found to be as follows :—

$$\left.\begin{aligned} g_{l,m}(1) &= \cos l\pi + i \sin l\pi \\ g_{l,m}(2) &= \cos\left(\frac{5l\pi}{3} + m\pi\right) + i \sin\left(\frac{5l\pi}{3} + m\pi\right) \\ g_{l,m}(3) &= -\cos\left(\frac{l\pi}{3} + \frac{2m\pi}{3}\right) - i \sin\left(\frac{l\pi}{3} + \frac{2m\pi}{3}\right) \\ g_{l,m}(4) &= -\cos\left(\frac{l\pi}{3} + \frac{5m\pi}{3}\right) - i \sin\left(\frac{l\pi}{3} + \frac{5m\pi}{3}\right) \end{aligned}\right\} \quad .. \quad (2, 9)$$

For the second adjoining plane ($x = -a/2$) the function f is given by

$$\begin{aligned} f_2(l, m) = {} & (\cos l\pi - i \sin l\pi) + [\cos(5l\pi/3 + m\pi) - \sin(5l\pi/3 + m\pi)] \\ & - [\cos(l\pi/3 + 2m\pi/3) - i \sin(l\pi/3 + 2m\pi/3) \\ & - [\cos(l\pi/3 + m\pi/3) - i \sin(l\pi/3 + 5m\pi/3)] \quad .. \quad (2, 10) \end{aligned}$$

From (2, 1), (2, 7), (2, 8) and (2, 9)

$$\Phi_j = \frac{2\pi}{b^2c^2} 4e^2 \sum_{l,m}{}' \frac{e^{-\alpha_{l,m}|x|}}{\alpha_{l,m}} \left(\sum_{k=1}^{4} \mathrm{F}_j^{l,m}(k) \right) .. \quad .. \quad .. \quad (2, 11)$$

Substituting this in (2, 3) and using (2, 5)

$$c_{11}^{e} = \frac{4\pi^2}{b^2c^2} 4e^2 \sum_{j=1}^{\infty} \left\{ \frac{\alpha_{l,m}|jd|}{2\pi} e^{-\alpha_{l,m}|jd|} \sum_{k=1}^{4} \left(\mathrm{F}_j^{l,m}(k) \right) \right\} \quad .. \quad (2, 12)$$

We put $\mathrm{F}_j{}^{|l,m|} = \sum_{k=1}^{4} \left\{ \mathrm{F}_j^{l,m}(k) + \mathrm{F}_j{}^{-l,-m}(k) \right\}$ .. .. (2, 13)

From Table I, it is apparent that the first three adjoining planes need only be considered. Substituting the final value from the table and the values of b and c from I, Table I

$$c_{11}^{e} = -\cdot 762 \times 10^{12} \text{ dynes/cm.}^2 \quad .. \quad .. \quad .. \quad .. \quad (2, 14)$$

The evaluation of c_{22}^{θ} is done on exactly similar lines ; the first three adjoining planes have to be considered. The value obtained is

$$c_{22}^{e\theta} = -\ 0{\cdot}608 \times 10^{12} \text{ dynes/cm.}^2 \quad .. \quad .. \quad .. \quad (2, 15)$$

TABLE I.

j	l'	m'	$\frac{\alpha_{l,m\|jd\|}}{2\pi}$	$e^{-\alpha_{f,m\|jd\|}}$	$\frac{\alpha_{l,m\|jd\|}}{2\pi} \times e^{-\alpha_{l,m\|jd\|}}$	$F_j{}^{\|l,m\|}$	$\frac{\alpha_{l,m\|jd\|}}{2\pi} e^{-\alpha_{l,m\|jd\|}} \times F_j{}^{\|l,m\|}$	
1	1	0	0·31	0·144	·044	− 18	− 0·792	
	0	1	0·43	0·067	·029	0	0	
	2	0	0·63	0·019	·011	18		+ 0·198
	1	1	0·74	0·009	·006	− 4	− 0·024	
	1	− 1	0·74	0·009	·006	− 4	− 0·024	
	0	2	0·86	0·0045	·004	12		+ 0·048
	3	0	0·94	0·003	·003	0	0	
	2	1	1·06	0·001	·001	6		+ 0·006
	2	− 1	1·06	0·001	·001	6		+ 0·006
2	1	0	0·63	0·019	·011	18		+ 0·198
	0	1	0·86	0·0045	·004	0	0	
3	1	0	0·94	·003	·003	− 18	− 0·054	
						TOTAL	− 0·894	+ 0·456
							− 0·438	

§3. *Nature of the Repulsive Forces.*

The potentials per unit cell of the crystal, due to the repulsive forces, as calculated in I with the help of the equilibrium condition, is given by $2\ \beta/\delta^n$ where, from I (3, 4)

$$\beta = \frac{a\ e^2}{n}\ \delta^{n-1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 1)$$

From I (3, 8) n was found to be 6·32 for aragonite.

Let the forces between two dis-similar ions be $\frac{b_{1,2}}{r^n}$, and between two similar radicals be $\frac{b_{11}}{r^n}$ or $\frac{b_{22}}{r^n}$. Let

$$b_{11} = b_{22} = -kb_{1,2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 2)$$

Each CO_3 ion is surrounded by 6 calcium ions projecting on the plane $z = 0$ into a hexagon and another 6 calcium ions projecting into an outer hexagon.

Of these twelve, two are situated at each of distances r_1, r_2, r_5, r_6, and one at each of r_3, r_4, r_7 and r_8, where the distances are given by :

$$\left.\begin{aligned} r_1^2 &= \frac{a^2}{4} + \frac{b^2}{36} + \frac{c^2}{9}; & r_5^2 &= a^2 + \frac{b^2}{9} + \frac{c^2}{36} \\ r_2^2 &= \frac{a^2}{4} + \frac{b^2}{36} + \frac{c^2}{36}; & r_6^2 &= a^2 + \frac{b^2}{9} + \frac{c^2}{9} \\ r_3^2 &= \frac{b^2}{9} + \frac{c^2}{36}; & r_7^2 &= \frac{4b^2}{9} + \frac{c^2}{36} \\ r_4^2 &= \frac{b^2}{9} + \frac{c^2}{9}; & r_8^2 &= \frac{4b^2}{9} + \frac{c^2}{9} \end{aligned}\right\} \quad .. \quad .. \quad (3, 3)$$

Each calcium ion is surrounded by 6 CO_3 ions projecting on the plane $z = 0$ into an isosceles triangle and another 6 CO_3 ions projecting into a larger isosceles triangle. The distances and the number of ions in the respective distances is the same as in (3, 3).

Besides, each calcium ion is surrounded by 14 calcium ions, of which 4 are at distance s_1, 2 at s_2 ; 2 at s_3 ; 4 at s_4 and 2 at s_5 ; and each CO_3 is surrounded by 14 CO_3 ions of which 2 are at s_3 and 4 at each of the distances s_6 ; s_7 and s_8 ; where the distances are given by :—

$$\left.\begin{aligned} s_1^2 &= \frac{a^2}{4} + \frac{b^2}{36} + \frac{c^2}{4}; & s_5^2 &= \frac{4b^2}{9} + \frac{c^2}{4} \\ s_2^2 &= \frac{b^2}{9} + \frac{c^2}{4}; & s_6^2 &= \frac{a^2}{4} + \frac{b^2}{4} + \frac{c^2}{36} \\ s_3^2 &= a^2; & s_7^2 &= \frac{a^2}{4} + \frac{b^2}{4} + \frac{c^2}{9} \\ s_4^2 &= \frac{a^2}{4} + \frac{b^2}{4}; & s_8^2 &= \frac{a^2}{4} + \frac{b^2}{4} + \frac{4c^2}{9} \end{aligned}\right\} \quad .. \quad .. \quad (3, 4)$$

Hence the potential per unit cell, due to the repulsive forces is given by

$$V_\Delta = 8\, b_{1,2} \left\{\frac{2}{r_1^n} + \frac{2}{r_2^n} + \frac{1}{r_3^n} + \frac{1}{r_4^n} + \frac{2}{r_5^n} + \frac{2}{r_6^n} + \frac{1}{r_7^n} + \frac{1}{r_8^n}\right.$$

$$\left. - k\left(\frac{2}{s_1^n} + \frac{1}{s_2^n} + \frac{2}{s_3^n} + \frac{2}{s_4^n} + \frac{1}{s_5^n} + \frac{2}{s_6^n} + \frac{2}{s_7^n} + \frac{2}{s_8^n}\right)\right\} \quad .. \quad (3, 5)$$

Expressing the lengths of these sides in terms of δ (I, 2, 22) and taking $n = 6 \cdot 32$ (I, Table III)

$$V_\Delta = \frac{8\, b_{1,2}}{\delta^{6 \cdot 32}} (447 \cdot 8 - k\, 80 \cdot 4) \quad .. \quad .. \quad .. \quad .. \quad (3, 6)$$

Comparing this with (3, 1)

$$2\, \frac{a\, e^2\, \delta^{5 \cdot 32}}{6 \cdot 32 \times \delta^{5 \cdot 32}} = 8\, \frac{b_{1,2}}{\delta^{6 \cdot 32}} (447 \cdot 8 - k\, 80 \cdot 4) \quad .. \quad .. \quad .. \quad (3, 7)$$

whence

$$b_{1,2} = \frac{a\, e^2\, \delta^{5 \cdot 32}}{4 \times 6 \cdot 32\, (447 \cdot 8 - k\, 80 \cdot 4)} \quad .. \quad .. \quad .. \quad .. \quad (3, 8)$$

Substituting this in (3, 5)

$$V_\Delta = \frac{2\, a\, e^2\, \delta^{5 \cdot 32}}{6 \cdot 32\, (447 \cdot 8 - k\, 80 \cdot 4)} \left\{\frac{2}{r_1^n} + \frac{2}{r_2^n} + \frac{1}{r_3^n} + \frac{1}{r_4^n} + \frac{2}{r_5^n} + \frac{2}{r_6^n} + \frac{1}{r_7^n} + \frac{1}{r_8^n}\right.$$

$$\left. - k\left(\frac{2}{s_1^n} + \frac{1}{s_2^n} + \frac{2}{s_3^n} + \frac{2}{s_4^n} + \frac{1}{s_5^n} + \frac{2}{s_6^n} + \frac{2}{s_7^n} + \frac{2}{s_8^n}\right)\right\} \quad .. \quad (3, 9)$$

The potential per unit volume is

$$V = \frac{1}{\delta^3} V_\Delta \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 10)$$

We take

$$c_{11}^{r} = \tfrac{1}{2} \frac{2a\, e^2\, \delta^{5\cdot32}}{6\cdot32\,(447\cdot8 - k\,80\cdot4)\,\delta^3} \left[\sum_{h=1}^{8} \left\{ t \frac{\partial^2}{\partial x^2}\left(\frac{1}{r_h^n}\right)\right\} x_h^2 - k \sum_{j=1}^{8} \left\{ \frac{\partial^2}{\partial x^2}\left(\frac{1}{s_j^n}\right)\right\} x_j^2 \right] \quad .. \quad (3, 11)$$

and $c_{2,2}^{r\theta} = \tfrac{1}{2} \frac{2a\, e^2\, \delta^{5\cdot32}}{6\cdot32\,(447\cdot8 - k\,80\cdot4)\,\delta^3} \times$

$$\left[\sum_{h=1}^{8} \left\{ t \frac{\partial^2}{\partial y_\theta^2}\left(\frac{1}{r_h^n}\right)\right\} y_{\theta h}^2 - k \sum_{j=1}^{8} \left\{ t \frac{\partial^2}{\partial y_\theta^2}\left(\frac{1}{s_j^n}\right)\right\} y_{\theta j}^2 \right] \quad .. \quad (3, 12)$$

where t is 1 or 2 according as in (3, 9) and x_h is the x-component of r_h, x_j the x-component of s_j and $y_{\theta,h}$ and $y_{\theta,j}$ are the y_θ components of r_h and s_j respectively.

The value of k is determined by comparison with the experimental value of c_{11}.

§4. *Evaluation of* k *and* $c_{22}^{r\theta}$.

Carrying out the differentiation and then substituting the numerical values of the r's and s's and their x-components in terms of δ

$$c_{11}^{r} = \frac{ae^2}{\delta^4\,(447\cdot8 - k\,80\cdot4)}\,(755\cdot6 - k\,85\cdot6) \quad .. \quad .. \quad (4, 1)$$

The value of c_{11}, as experimentally determined by W. Voigt,[3] is $1\cdot6 \times 10^{12}$ dynes/cm.^{2}

From (1, 9) and (2, 14)

$$c_{11}^{r} = 2\cdot362 \times 10^{12} \text{ dynes/cm.}^2 \quad .. \quad .. \quad .. \quad .. \quad (4, 2)$$

Substituting the numerical values and comparing (4, 1) and (4, 2)

$$2\cdot362 = \frac{1\cdot105}{447\cdot8 - k \times 80\cdot4}\,(755\cdot6 - k\,85\cdot6) \quad .. \quad .. \quad (4, 3)$$

whence $k = 2\cdot36$ .. .. (4, 4)

From (3, 12) we get by numerical simplification

$$c^{r\theta} = 1\cdot756 \times 10^{12} \text{ dynes/cm.}^2 \quad .. \quad .. \quad .. \quad .. \quad (4, 5)$$

whence from (1, 9) and (2, 15)

$$c_{22}^{\theta} = 1\cdot148 \times 10^{12} \text{ dynes/cm.}^2 \quad .. \quad .. \quad .. \quad .. \quad (4, 6)$$

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[3] W. Voigt, *Ann. de Phy.*, 1907, **24**, 290.

§5. *Comparison with the Experimental Value.*

The value of the elasticity-constant in the direction Oy_θ is not directly determined. With the help of the transformation formula for the elasticity-constants[4] we get

$$c_{22}^{\theta} = c_{11} \sin^4\theta + c_{22} \cos^4\theta + 2 \cos^2\theta \sin^2\theta \, (c_{12} + 2\, c_{66}) \quad .. \quad .. \quad (5, 1)$$

Substituting the values of the elasticity-constants from W. Voigt's measurements and the values of the trigonometric terms derived from (1, 1), we get

$$c_{22}^{\theta} = 1 \cdot 021 \times 10^{12} \text{ dynes/cm.}^2 \quad .. \quad .. \quad .. \quad .. \quad (5, 2)$$

The agreement between the two values given in (4, 6) and (5, 2) is quite satisfactory.

I wish to express my thanks to Prof. M. Born for his guidance in this work.

Summary.

The elasticity-constant c_{jh} consists of two parts c_{jh}^{e}, due to the electrostatic forces and c_{jh}^{r} due to the repulsive forces. Considering the crystal as built up of a system of parallel neutral planes, the electro-static part of the elasticity-constant in a direction perpendicular to the system of planes, can be determined by considering the action on any one of the system of planes, of a few of its adjoining planes on one of its sides. c_{11}^{e} and $c_{22}^{e\,\theta}$ are determined in this way. The nature of the repulsive forces is completely determined by the equilibrium condition and by comparison with the experimental value of c_{11}. The value of $c_{22}^{r\,\theta}$ is then determined. The theoretical and experimental values of c_{22}^{θ} are found to agree well.

[4] W. Voigt, *Lehrbuch der Kristallphysik*, §291, p. 595.

LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part III. Lattice-Energy of the Crystals of Calcite and Its Thermo-Chemical Applications.

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Introduction.

In two recent papers by the author,[1] referred to hereafter as I and II, the Lattice-Energy and the elasticity constants of the orthorhombic crystals of Aragonite were calculated. In this and the next part, we deal on exactly similar lines with the crystals of calcite. Thus calcite is assumed to be a polar compound composed of C_a^{++} and CO_3^{--} ions; the forces being the electro-static repulsions and attractions and the "repulsive forces" of the type b/r^n.

On calculating the lattice-energy of the crystal, we obtain the value of 'n' with the help of the compressibility measurements.

§1. *The Electro-Static Energy Density.*

The crystals of calcite[2] belong to the trigonal system, and possess hexagonal symmetry. Taking the z-axis, along the trigonal axis and the x- and y-axes in a plane perpendicular to it, so that the "Grund-vectors" (I §1) will have the components

$$a_x = 4{\cdot}98, \quad b_y = \sqrt{3}\ a_x, \quad c_z = 8{\cdot}55 \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1, 1)$$

the other components being zero.

The only surviving components of the "Grund-vectors" of the reciprocal lattice are

$$a'_x = \frac{1}{a_x}, \quad b'_y = \frac{1}{b_y}, \quad c'_z = \frac{1}{c_z} \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1, 2)$$

The vector $\vec{q^l}$ [I (1, 15)] will have the components

$$\vec{q^l} = 2\pi \left(\frac{l_1}{a_x}, \ \frac{l_2}{b_y}, \ \frac{l_3}{c_z} \right) \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1, 3)$$

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[1] B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1 and 514.

[2] Wycoff, *The Structure of Crystals*, Second Edition, p. 273; or "Zeitschrift fur Kristallographie," *Struktur Bericht*, 1913–26, p. 292.

The electro-static energy density is given by

$$U_{\Delta} = \frac{1}{2\Delta}\,\phi_0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 4)$$

where $\phi_0 = \overline{\psi}\,(0) \sum_{k'} e_{k'}{}^2 + \sum_{kk'} e_k\, e_{k'}\, \psi\,(r_{kk'})$ .. .. .. (1, 5)

$\overline{\psi}\,(0)$ and $\psi\,(r_{kk'})$ are defined in I (1, 7) (1, 8) (1, 9) and (1, 10).

(i) Evaluation of $\overline{\psi}\,(0)$.—

From I (2, 6) we have

$$\overline{\psi}_1\,(0) = \frac{b^3}{\pi\, abc} \sum_{l}{}' \frac{e^{-\left(l_1{}^2 \frac{b^2}{a^2} + l_2{}^2 + l_3{}^2 + \frac{b^2}{c^2}\right)}}{\left(l_1{}^2 \frac{b^2}{a^2} + l_2{}^2 + l_3{}^2 \frac{b^2}{c^2}\right)} - \frac{2\sqrt{\pi}}{b} \quad .. \quad (1, 6)$$

As in I, we need consider only the first few terms, since the expression under the sign of summation is rapidly converging.

In this case we have

$$\frac{b^2}{a^2} = 3 \quad \text{and} \quad \frac{b^2}{c^2} = 1{\cdot}018 \quad .. \quad .. \quad .. \quad .. \quad (1, 7)$$

We write

$$3\, l_1{}^2 + l_2{}^2 + 1{\cdot}018\, l_3{}^2 = \lambda_{l_1, l_2, l_3} \quad .. \quad .. \quad .. \quad .. \quad (1, 8)$$

TABLE I.

l_1	l_2	l_3	λ_{l_1, l_2, l_3}	$e^{-\lambda_{l_1, l_2, l_3}}$	$\frac{e^{-\lambda_{l_1, l_2, l_3}}}{\lambda_{l_1, l_2, l_3}}$	$P(l_1, l_2, l_3)$	$P\,\frac{e^{-\lambda}}{\lambda}$
1	0	0	3	·0497	·0166	2	·0322
0	1	0	1	·3676	·3676	2	·7352
0	0	1	1·018	·3614	·3550	2	·7100
2	0	0	12	..	..	..	..
0	2	0	4	·0183	·0046	2	·0092
0	0	2	4·072	·0177	·0043	2	·0086
1	1	0	4	·0183	·0046	4	·0176
0	1	1	2·018	·1326	·0658	4	·2632
1	0	1	4·018	·0179	·0044	4	·0176
0	2	1	5·018	·0066	·0013	4	·0052
0	1	2	5·072	·0062	·0012	4	·0048
1	1	1	5·018	·0066	·0013	8	·0104
						Sum	1·8140

The 7th column gives the number of different combinations for the same numerical values of l_1, l_2, l_3; thus for $|l_1| = 1$, $|l_2| = 1$, and $l_3 = 0$ we have the following 4 combinations:

$$(1, 1, 0);\ (-1, 1, 0);\ (1, -1, 0);\ (-1, -1, 0).$$

Hence

$$\bar{\psi}_1(0) = \frac{b^2}{\pi abc} 1{\cdot}8140 - \frac{2\sqrt{\pi}}{b} \quad .. \quad .. \quad .. \quad .. \quad (1, 9)$$

$$= \frac{{\cdot}556 \times 1{\cdot}814 - 3{\cdot}544}{b} \quad .. \quad .. \quad .. \quad .. \quad (1, 10)$$

Now

$$\bar{\psi}_2(0) = \sum_{l}{}' \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{\pi}{b} r^l} e^{-a^2}\, da}{r^l} - \frac{b^2}{\pi abc} \quad .. \quad .. \quad (1, 11)$$

The contribution from the first term, containing the integral, is negligible.

$$\therefore\ \bar{\psi}_2(0) = -\frac{b/a \times b/c}{\pi b} \quad .. \quad .. \quad .. \quad .. \quad (1, 12)$$

$$= -\frac{{\cdot}556}{b} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 13)$$

From (1, 13) and (1, 10)

$$\bar{\psi}(0) = -\frac{3{\cdot}091}{b} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 14)$$

(ii) Evaluation of $\sum_{kk'} e_k\, e_{k'}\, \psi(r_{kk'})$.—

A unit cell of the crystal consists of 6 molecules of the carbonates. The calcium ions are situated at

$$(0, 0, 0);\ \left(\frac{a}{2}, \frac{b}{2}, 0\right);\ \left(0, \frac{b}{3}, \frac{c}{3}\right);\ \left(\frac{a}{2}, \frac{5b}{6}, \frac{c}{3}\right)$$

$$\left(0, \frac{2b}{3}, \frac{2}{3}\right) \text{ and } \left(\frac{a}{2}, \frac{b}{6}, \frac{2c}{3}\right) \quad .. \quad .. \quad .. \quad .. \quad (1, 15)$$

$$\left(0, \frac{2b}{3}, \frac{c}{6}\right);\ \left(\frac{a}{2}, \frac{b}{6}, \frac{c}{6}\right);\ \left(0, 0, \frac{c}{2}\right);\ \left(\frac{a}{2}, \frac{b}{2}, \frac{c}{2}\right)$$

$$\left(0, \frac{b}{3}, \frac{5c}{6}\right) \text{ and } \left(\frac{a}{2}, \frac{5b}{6}, \frac{5c}{6}\right) \quad .. \quad .. \quad .. \quad .. \quad (1, 16)$$

From I (2, 15)

$$\psi(r_{kk'}) = \frac{4\pi}{abc} \sum_{l}{}' \frac{e^{2\pi i \left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c}\right)}}{4\pi^2 \left(l_1^2 \frac{1}{a^2} + l_2^2 \frac{1}{b^2} + l_3^2 \frac{1}{c^2}\right)} \quad .. \quad .. \quad (1, 17)$$

where $x_{kk'}$, $y_{kk'}$ and $z_{kk'}$ are the projections of $r_{kk'}$ on the three co-ordinate axes.

Hence

$$\sum_{kk'} e_k\, e_{k'} \psi\,(r_{kk'}) = \frac{b^2}{\pi\, abc} \sum_{l}{}' \sum_{kk'} e_k\, e_{k'}\, \frac{e^{2\pi i \left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c}\right)}}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2}\right)} \quad .. \quad (1, 18)$$

Expressing the exponential as a cosine function this can be written as

$$\sum_{kk'} e_k\, e_{k'}\, \psi\,(r_{kk'}) = \frac{b^2}{\pi\, abc} \sum_{l'}{}' \sum_{kk'} \frac{2 \cos\left(l_1' \frac{x_{kk'}}{a} + l_2' \frac{y_{kk'}}{b} + l_3' \frac{z_{kk'}}{c}\right)}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2}\right)} \quad .. \quad (1, 19)$$

The dashes over the l's denote that if a certain set of values, say $(\bar{l}_1, \bar{l}_2, \bar{l}_3)$ is taken, we need not consider the set $(-\bar{l}_1, -\bar{l}_2, -\bar{l}_3)$. Any other set like $(\bar{l}_1, -\bar{l}_2, -\bar{l}_3)$ or $(\bar{l}_1, -\bar{l}_2, \bar{l}_3)$ has, however, to be considered.

The co-ordinates of the 12 points in a unit cell are given in (1, 15) and (1, 16) from which the values of $x_{kk'}$ etc., are obtained. Substituting these and associating a change $+2e$ with each calcium ions and a charge $-2e$ with each CO_3 ions, we obtain

$$\sum_{kk'} e_k\, e_{k'} \psi\,(r_{kk'}) = \frac{b/a \times b/c}{\pi b}\, 4e^2 \times 4 \sum_{l'}{}' \frac{\mathrm{F}\,\{\cos\,(l_1', l_2', l_3')\,\pi\}}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3 \frac{b^2}{c^2}\right)} \quad .. \quad (1, 20)$$

where the function F is given by

$$\begin{aligned}
\mathrm{F} = {} & 4 \cos\,(l_1 + l_2)\,\pi + 2 \cos\,(l_1 - l_2)\,\pi + 2 \cos\left(\frac{4\,l_2}{3} + \frac{4\,l_3}{3}\right)\pi \\
& + 6 \cos\left(\frac{2\,l_2}{3} + \frac{2\,l_3}{3}\right)\pi + 2 \cos\left(\frac{4\,l_2}{3} - \frac{2\,l_3}{3}\right)\pi + 2 \cos\left(\frac{2\,l_2}{3} - \frac{4\,l_3}{3}\right)\pi \\
& + 4 \cos\left(l_1 + \frac{l_2}{3} - \frac{2\,l_3}{3}\right)\pi + 2 \cos\left(l_1 - \frac{l_2}{3} + \frac{2\,l_3}{3}\right)\pi + 2 \cos\left(l_1 - \frac{l_2}{3} - \frac{4\,l_3}{3}\right)\pi \\
& + 2 \cos\left(l_1 + \frac{l_2}{3} + \frac{4\,l_3}{3}\right)\pi + 2 \cos\left(l_1 + \frac{5\,l_2}{3} + \frac{2\,l_3}{3}\right) \\
& - \Big\{6 \cos l_3\pi + 4 \cos\left(\frac{4\,l_2}{3} + \frac{l_3}{3}\right)\pi + 6 \cos\left(\frac{2\,l_2}{3} - \frac{l_3}{3}\right)\pi \\
& + 2 \cos\left(\frac{2\,l_2}{3} + \frac{5\,l_3}{3}\right)\pi + 2 \cos\,(l_1 + l_2 + l_3)\,\pi + 2 \cos\,(l_1 + l_2 - l_3)\,\pi \\
& + \cos\,(l_1 - l_2 - l_3)\,\pi + \cos\,(l_1 - l_2 + l_3)\,\pi + 4 \cos\left(l_1 - \frac{l_2}{3} - \frac{l_3}{3}\right)\pi \\
& + 5 \cos\left(l_1 + \frac{l_2}{3} + \frac{l_3}{3}\right)\pi + \cos\left(l_1 + \frac{5\,l_2}{3} + \frac{5\,l_3}{3}\right)\pi \\
& + \cos\left(l_1 + \frac{l_2}{3} - \frac{5\,l_3}{3}\right)\pi + \cos\left(l_1 + \frac{5\,l_2}{3} - \frac{l_3}{3}\right)\pi \Big\} \quad .. \qquad .. \quad (1, 21)
\end{aligned}$$

Carrying out the summation until the denominator becomes sufficiently large to neglect the subsequent terms, we obtain

$$\Sigma\, e_k\, e_{k'} \psi\,(r_{kk'}) = -\frac{\cdot 556}{b}\, 16\, e^2\, (16 \cdot 18) \quad .. \quad .. \quad .. \quad (1, 22)$$

Substituting the values from (1, 14) and (1, 22) in (1, 5) we get

$$\phi_0 = -\frac{4\, e^2}{b}\, (37 \cdot 09 + 35 \cdot 98) \quad .. \quad .. \quad .. \quad .. \quad (1, 23)$$

Defining

$$\delta^3 = abc \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 24)$$

So that from (1, 1)

$$\delta = \frac{1}{1 \cdot 205}\, b \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 25)$$

(1, 23) can be written as

$$\phi_0 = -\frac{e^2}{\delta}\, 242 \cdot 6 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 26)$$

or $$\phi_0 = -2\,\frac{e^2}{\delta}\, \alpha \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 27)$$

where $$\alpha = 121 \cdot 3 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 28)$$

§2. *The Lattice-Energy.*

For the stability of the crystals, repulsive forces of the type b/r^n, besides the electro-static attractions and repulsions, have to be assumed. With these additional forces the function ϕ_0 given in (1, 27) will be of the form

$$\phi_0 = -2\left(\alpha\,\frac{e^2}{\delta} - \frac{\beta}{\delta^n}\right) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 1)$$

The " Lattice-Energy " per one mole of the substance is defined by

$$U = -\frac{1}{2z}\, N\, \phi_0$$

$$= \frac{1}{z}\, N \left(\alpha\,\frac{e^2}{\delta} - \frac{\beta}{\delta^n}\right) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 2)$$

where z is the number of molecules per unit cell of the crystal and N is Avogadro's number.

Proceeding as in I [refer equations I (3, 3), (3, 4)....(3, 9)] we get

$$n = 1 + \frac{9}{\alpha e^2 \chi}\left(\frac{Mz}{N\rho}\right)^{\frac{4}{3}} \quad .. \quad .. \quad .. \quad .. \quad (2, 3)$$

and $$U = \left(1 - \frac{1}{n}\right) \alpha\, e^2 \left(\frac{N}{z}\right)^{\frac{4}{3}} \left(\frac{\rho}{M}\right)^{\frac{1}{3}} \quad .. \quad .. \quad .. \quad .. \quad (2, 4)$$

where χ is the compressibility, M the molecular weight and ρ the density of calcite.

TABLE II.

$\frac{1}{\chi \times 10^{12}}$ dynes/cm.^{2} experimental	Source[3]	n Calculated	U Calculated
1/1·34	1	7·3	803·3
1/1·39	2	7·1	799·5
1/1·52	3	6·5	782·0

The energy values are expressed in k. cal.

§3. *The Thermo-Chemical Cycle.*

Exactly as in I §4, the calculated value of the " Lattice-Energy " can be verified by a thermo-chemical cycle, quite similar to that in I. The heat of formation of calcite is 231·8 k. cal.[4] With the same notation as in I (4, 2), (4, 3) and (4, 4) we get

$$B = 879{\cdot}0 \text{ k. cal.} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 1)$$

by taking the last value of U from Table II ;

$$A = 949{\cdot}1 \text{ k. cal.} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 2)$$

so that $X = 70{\cdot}1$ k. cal. .. .. (3, 3)

The value of X in the case of Aragonite was obtained as 135·5 k. cal. Considering the various infinite summations and the uncertainty in the values of the compressibilities involved in the evaluation of X, this much agreement in the two values is not quite unsatisfactory.

Summary.

The lattice-energy of the crystals of calcite is calculated ; and the value of n the index of the repulsive forces is determined with the help of the compressibility measurements. The value of the lattice-energy is applied to a thermo-chemical cyclic process.

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[3] 1. Madelung and Fuchs. 2. Adams and Williamson. 3. W. Voigt.
All the values are given together in Mellor's *Inorganic and Physical Chemistry*. There are similar discrepancies in the compressibility measurements of Aragonite also.

[4] *Handbook of Chemistry and Physics*, Hodgman-Lange, Fifth Edition.

ON THE FLEXURE OF A HOLLOW SHAFT—I.

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Saint-Venant's flexure problem has been solved only in a limited number of cases. All the cross-sections discussed by Saint-Venant, and many writers after him possess bi-axial symmetry, there being an axis of symmetry in the plane of loading and also an axis perpendicular to this plane. But more often than not we come across sections in engineering problems which have only uni-axial symmetry, and these have received attention from very few authors.[1] The present paper deals with the flexure-solution of a hollow shaft with a cavity placed excentrically.[2] The torsion solution for this section has been already obtained by Macdonald.[3]

In the case of uni-axial symmetry we can have the axis of symmetry (1) perpendicular to the plane of loading, (2) in the plane of loading. We propose to deal with the two cases one after the other.

(1) *Axis of symmetry perpendicular to the plane of loading*—

The transformation we require for our purpose is

$$x + iy = c \tan \tfrac{1}{2}(\xi + i\eta), \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

which gives rise to the two families of circles

$$x^2 + (y - c \coth \eta)^2 = c^2 \operatorname{cosech}^2 \eta,$$

and $$(x + c \cot \xi)^2 + y^2 = c^2 \operatorname{cosec}^2 \xi,$$

the η-family being the one which enables us to take the two circles of the cross-section, shewn in Fig. 1, as $\eta = \alpha$, and $\eta = \beta$, α being greater than β.

---

[1] Young, Elderton and Pearson have been the first to discuss such cases in *Draper's Company Research Memoirs*, Technical Series, 1918, No. 7. When the axis of symmetry is in the plane of loading, Seeger and Pearson have obtained a solution in *Proc. Roy. Soc.*, 1920, **96A**, 211. Recently, we have treated a few more cases in *Proc. Lond. Math. Soc.*, 1934, **37** (2), 502, and in forthcoming papers in *Phil. Mag.* and *Proc. Lond. Math. Soc.*

[2] The problem has been suggested as a soluble one by Love in his *Mathematical Theory of Elasticity* (4th Edition), 1927, p. 340.

[3] *Cf.* Love, *Mathematical Theory of Elasticity*, Fourth Edition, p. 320.

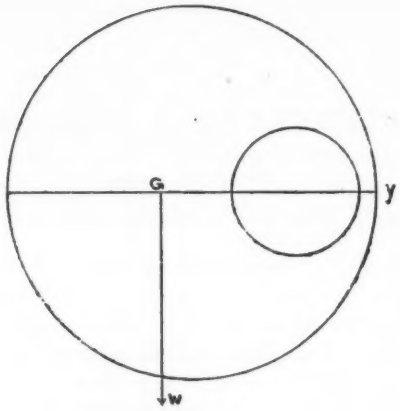

FIG. 1.

The weight W is supposed to act along a line through G parallel to the x-axis. If a, b are the radii of the two circles, and k the distance between their centres, we have the relations

$$c^2 = a^2 \sinh^2 \alpha = b^2 \sinh^2 \beta,$$
$$4c^2 = (b^2 - a^2)^2/k^2 + k^2 - 2(a^2 + b^2).$$

x and y are given from (1) by the equations

$$x = \frac{c \sin \xi}{\cos \xi + \cosh \eta}, \quad y = \frac{c \sinh \eta}{\cos \xi + \cosh \eta} \qquad .. \qquad .. \qquad (2)$$

The present case involves what is called the " associated flexual torsion". So we should write the components of displacement and stress as

$$u = -\tau yz + \frac{W}{EI}\left[\tfrac{1}{2}\sigma(l - z)\{x^2 - (y - \bar{y})^2\} + \tfrac{1}{2} lz^2 - \tfrac{1}{6} z^3\right] + \beta_1 z + \alpha_1, \quad .. \quad .. \quad .. \quad (3.1)$$

$$v = \tau zx + \frac{W}{EI}\sigma x (l - z)(y - \bar{y}), \qquad .. \qquad .. \qquad .. \qquad (3.2)$$

$$w = \tau\phi + \frac{W}{EI}\left[\chi(x, y) - x(lz - \tfrac{1}{2} z^2) - x(y - \bar{y})^2\right] - \beta_1 x + \gamma_1, \qquad .. \qquad .. \qquad (3.3)$$

$$\widehat{yz} = \mu\tau\left(\frac{\partial\phi}{\partial y} + x\right) + \frac{\mu W}{EI}\left[\frac{\partial\chi}{\partial y} - (2 + \sigma) x (y - \bar{y})\right], \quad .. \quad (4.1)$$

$$\widehat{xz} = \mu\tau\left(\frac{\partial\phi}{\partial x} - y\right) + \frac{\mu W}{EI}\left[\frac{\partial\chi}{\partial x} - \tfrac{1}{2}\sigma x^2 - (1 - \tfrac{1}{2}\sigma)(y - \bar{y})^2\right] \qquad .. \quad (4.2)$$

$$\widehat{zz} = -\frac{W}{I} x (l - z), \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4.3)$$

$$\widehat{xx} = \widehat{yy} = \widehat{xy} = 0, \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4.4)$$

where $\chi(x, y)$ is the flexure function, ϕ the torsion function, I the moment of inertia of the cross-sections about an axis through G parallel to the y-axis, l the length of the beam, and τ, α_1, β_1, τ_1, γ_1 are constants.

The boundary condition

$$\widehat{xz}\cos(x\gamma) + \widehat{yz}\cos(y\gamma) = 0 \qquad \ldots \qquad \ldots \qquad \ldots \qquad (5)$$

gives

$$\left[\frac{\partial \chi}{\partial x} - \tfrac{1}{2}\sigma x^2 - (1 - \tfrac{1}{2}\sigma)(y - \bar{y})^2\right]\cos(x\gamma) + \left[\frac{\partial \chi}{\partial y} - (2+\sigma)\, x\,(y - \bar{y})\right]\cos(y\gamma) = 0, \qquad (6)$$

which if we put

$$\chi = \chi_1 + \sigma\,\bar{y}\,\phi + (1 - \tfrac{1}{2}\sigma)\,\bar{y}^2 x - 2\,\bar{y}\,x\,y, \qquad \ldots \qquad \ldots \qquad (7)$$

and assume ψ_1 to be the hormonic conjugate function of χ_1, becomes

$$\frac{\partial \psi_1}{\partial \xi} = [\tfrac{1}{2}\sigma x^2 + (1 - \tfrac{1}{2}\sigma)\, y^2]\,\frac{\partial y}{\partial \xi} - (2+\sigma)\, x\, y\,\frac{\partial x}{\partial \xi}. \qquad \ldots \qquad (8)$$

A little calculation gives

$$\int x^2 \frac{\partial y}{\partial \xi}\, d\xi = c^3 \sinh\eta \int \frac{\sin^3\xi\, d\xi}{(\cos\xi + \cosh\eta)^4}$$

$$= -\tfrac{2}{3} c^2 y + \tfrac{1}{3} x^2 y + \tfrac{1}{3}\frac{c^3 \sinh\eta\cosh\eta}{(\cos\xi + \cosh\eta)^2},$$

$$\int xy\,\frac{\partial x}{\partial \xi}\, d\xi = \tfrac{1}{2} x^2 y - \tfrac{1}{2}\int x^2 \frac{\partial y}{\partial \xi}\, d\xi,$$

and

$$3x^2 y - y^3 = -4y^3 - 3\,c^2 y + \frac{6\,c^3 \sinh\eta\cosh\eta}{(\cos\xi + \cosh\eta)^2}.$$

Hence we can write

$$\tfrac{1}{2}\sigma \int x^2 \frac{\partial y}{\partial \xi}\, d\xi + \tfrac{1}{3}(1 - \tfrac{1}{2}\sigma)\, y^3 - (2+\sigma)\int xy\,\frac{\partial x}{\partial \xi}\, d\xi$$

$$= -\tfrac{1}{4} c^2 (3 + 2\sigma)\, y - \tfrac{1}{4}(3x^2 y - y^3) + \tfrac{1}{3}\frac{c^3 \sinh\eta\cosh\eta}{(\cos\xi + \cosh\eta)^2}. \qquad \ldots \qquad (9)$$

Comparing (9) with (8) we see that we should express

$$\sinh\eta\cosh\eta/(\cos\xi + \cosh\eta)^2$$

in a Fourier's series in ξ. To simplify we write

$$\psi_1 = -\tfrac{1}{4} c^2 (3 + 2\sigma)\, y - \tfrac{1}{4}(3x^2 y - y^3) + \tfrac{1}{2} c^3 \psi_2$$

Assuming

$$\psi_2 = \sum_{n=1}^{\infty} [A_n \operatorname{Sinh} n(\eta - \alpha) + B_n \operatorname{Sinh} n(\beta - \eta)]\cos n\xi,$$

we see that the new boundary condition

$$\psi_2 = \frac{\sinh \eta \cosh \eta}{(\cos \xi + \cosh \eta)^2} + f(\eta) \quad .. \quad .. \quad .. \quad (10)$$

gives over $\eta = a$

$$\frac{\sinh a \cosh a}{(\cos \xi + \cosh a)^2} + f(a) = \sum_{n=1}^{\infty} B_n \sinh n(\beta - a) \cos n \xi, \quad (11)$$

where the constant $f(a)$ is given by

$$f(a) = -\frac{1}{2\pi} \int_{-\pi}^{+\pi} \frac{\sinh a \cosh a}{(\cos \xi + \cosh a)^2} d\xi$$

$$= \frac{1}{\pi} \cosh a \frac{d}{da} \int_{0}^{\pi} \frac{d\xi}{\cos \xi + \cosh a} = -\coth^2 a.$$

Hence $f(\eta)$ should be taken equal to $-\coth^2 \eta$ in (10). The general coefficient B_n in (11) is given by

$$B_n = \frac{\sinh a \cosh a}{\pi \sinh n(\beta - a)} \int_{-\pi}^{+\pi} \frac{\cos n \xi}{(\cos \xi + \cosh a)^2} d\xi \quad .. \quad (12.1)$$

In like manner by considering (10) for $\eta = \beta$ we get

$$A_n = \frac{\sinh \beta \cosh \beta}{\pi \sinh n(\beta - a)} \int_{-\pi}^{+\pi} \frac{\cos n\xi}{(\cos \xi + \cosh \beta)^2} d\xi \quad .. \quad (12.2)$$

It should be mentioned here the a term $D\eta$, where D is an arbitrary constant, can be added to the expression for ψ_2. χ will now get a term $D\xi$, and hence the w-displacement will become many-valued. To secure a one valued expression for w it would be necessary to put $D = 0$. A similar result holds good for any hollow shaft.

Now

$$A_n = -\frac{\cosh \beta}{\pi \sinh n(\beta - a)} \frac{\partial}{\partial \beta} \int_{-\pi}^{+\pi} \frac{\cos n \xi}{\cos \xi + \cosh \beta} d\xi$$

$$= -\frac{\cosh \beta}{\pi \sinh n(\beta - a)} \frac{\partial}{\partial \beta} \left[\frac{2h}{1 - h^2} \int_{-\pi}^{+\pi} \frac{1 - h^2}{1 + 2h \cos \xi + h^2} \cos n \xi \, d\xi \right]$$

$$(h = e^{-\beta})$$

$$= -\frac{\cosh \beta}{\pi \sinh n(\beta - a)} \frac{\partial}{\partial \beta} \left[\frac{2(-1)^n \pi e^{-n\beta}}{\sinh \beta} \right]$$

$$= (-1)^n \frac{2 \cosh \beta}{\sinh n(\beta - a)} \cdot \frac{n \sinh \beta + \cosh \beta}{\sinh^2 \beta} e^{-n\beta} \quad .. \quad (13.1)$$

In like manner

$$B_n = (-1)^n \frac{2\cosh\alpha}{\sinh n(\beta-\alpha)} \cdot \frac{n\sinh\alpha+\cosh\alpha}{\sinh^2\alpha} e^{-n\alpha} \quad .. \quad (13.2)$$

Thus we have

$$\psi_2 = 2\sum_1^\infty \frac{(-1)^n}{\sinh n(\beta-\alpha)} e^{-n\alpha}[\coth\alpha(n+\coth\alpha)\sinh n(\beta-\eta) + e^{-n\beta}\coth\beta(n+\coth\beta)\sinh n(\eta-\alpha)]\cos n\xi, \quad (14)$$

and

$$\chi = \bar{\sigma} y\phi + x[(1-\tfrac{1}{2}\sigma)y^2 - \tfrac{1}{4}c^2(3+2\sigma)] - 2\bar{y}xy - \tfrac{1}{4}(x^3-3xy^2) + \tfrac{1}{2}c^3\sum_{n=1}^\infty [A_n\cosh n(\eta-\alpha) - B_n\cosh n(\beta-\eta)]\sin n\xi \quad .. \quad .. \quad (15)$$

The value of the torsion function ϕ is known to be given by

$$\phi = 2c^2\sum_{n=1}^\infty \frac{(-1)^n\sin n\xi}{\sinh n(\beta-\alpha)}[e^{-n\beta}\coth\beta\cosh n(\eta-\alpha) - e^{-n\alpha}\coth\alpha\cosh n(\beta-\eta)] \quad .. \quad .. \quad .. \quad .. \quad (16)$$

and, if Ω be its conjugate harmonic function, the boundary condition satisfied by Ω is

$$\Omega = \tfrac{1}{2}(x^2+y^2) + c^2(\tfrac{1}{2} - \coth\eta) \quad .. \quad .. \quad .. \quad (17)$$

Presently we shall need these results.

As regards the convergency of the infinite services in (15) we observe that both $\sinh n(\eta-\alpha)/\sinh n(\beta-\alpha)$ and $\cos n\xi$ are less than unity in the region enclosed by the circles $\eta=\alpha$ and $\eta=\beta$. The series $\sum_1^\infty (-1)^n e^{-n\alpha}$ and $\sum_1^\infty (-1)^n n e^{-n\alpha}$ being both convergent, the convergency of the series in (15) follows at once.

Determination of τ.

To determine τ we have the equation

$$-W\bar{y} = \iint (xyz - yxz)\,dxdy \quad .. \quad .. \quad .. \quad (17.1)$$

the double integral being taken over the area of a cross-section. Substituting the values of yz and xz we get

$$-W\bar{y} = \mu\left(\tau + \frac{\bar{\sigma}yW}{EI}\right)\iint\left(x^2+y^2 - x\frac{\partial\Omega}{\partial x} - y\frac{\partial\Omega}{\partial y}\right)dxdy - \tfrac{1}{2}\frac{\mu c^3 W}{EI}\iint\left(x\frac{\partial\psi_2}{\partial x} + y\frac{\partial\psi_2}{\partial y}\right)dxdy$$

$$+ \tfrac{1}{4} \frac{\mu c^2 w}{EI} (3 + 2\sigma) \iint y \, dxdy$$

$$+ \tfrac{1}{4} \frac{\mu W}{EI} (1 - 2\sigma) \iint y (x^2 + y^2) \, dxdy \quad .. \quad (17.2)$$

By Green's theorem

$$\iint \left(x \frac{\partial \Omega}{\partial x} + y \frac{\partial \Omega}{\partial y} \right) dxdy = - \tfrac{1}{2} \int r^2 \frac{\partial \Omega}{\partial n} \, ds,$$

where $r^2 = x^2 + y^2$, ∂n an element of the inward drawn normal, and the line integral is to be taken for the circles $\eta = \alpha$ and $\eta = \beta$ in opposite senses.

Now

$$\int r^2 \frac{\partial \Omega}{\partial n} \, ds = \int_{-\pi}^{\pi} r^2 \frac{\partial \Omega}{\partial \eta} \, d\xi = c^2 \int_{-\pi}^{\pi} \left(\frac{2 \cosh \eta}{\cos \xi + \cosh \eta} - 1 \right) \frac{\partial \Omega}{\partial \eta} \, d\xi.$$

Putting the value of Ω, and evaluating the resulting integrals as in (13), we get

$$\iint \left(x \frac{\partial \Omega}{\partial x} + y \frac{\partial \Omega}{\partial y} \right) dxdy$$

$$= 8 \pi c^4 \coth \alpha \coth \beta \sum_1^\infty \left[\frac{n e^{-n(\alpha+\beta)}}{\sinh n (\beta - \alpha)} \right]$$

$$- 4 \pi c^4 \sum_1^\infty n \coth n (\beta - \alpha) \{ \coth^2 \beta \, e^{-2n\beta} + \coth^2 \alpha \, e^{-2n\alpha} \}$$

$$= \pi (b^2 - a^2) (a^2 + b^2 + c^2) - 4 \pi c^4 (\coth \alpha - \coth \beta)^2 \times$$

$$\times \sum_1^\infty \frac{n e^{-n(\alpha+\beta)}}{\sinh n (\beta - \alpha)} \quad .. \quad .. \quad .. \quad (18)$$

Also

$$\iint (x^2 + y^2) \, dxdy = \pi (b^2 - a^2) [c^2 + \tfrac{3}{4} (b^2 + a^2)].$$

Proceeding as in (18) we get

$$\iint x \frac{\partial \psi_2}{\partial x} + y \frac{\partial \psi_2}{\partial y} \, dxdy$$

$$= 4 \pi c^2 \coth \alpha \coth \beta \sum_1^\infty \frac{n e^{-n(\alpha+\beta)}}{\sinh n (\beta - \alpha)} (2n + \coth \alpha + \coth \beta)$$

$$- 4 \pi c^2 \sum_1^\infty n \coth n (\beta - \alpha) e^{-2n\beta} \coth^2 \beta (n + \coth \beta)$$

$$- 4 \pi c^2 \sum_1^\infty n \coth n (\beta - \alpha) e^{-2n\alpha} \coth^2 \alpha (n + \coth \alpha) \quad (19)$$

But

$$e^{-2n\beta}\coth n(\beta-\alpha) = \frac{e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)} - e^{-2n\beta}$$

$$e^{-2n\alpha}\coth n(\beta-\alpha) = \frac{e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)} + e^{-2n\alpha}$$

$$c^4 \sum_1^\infty n\, e^{-2n\beta} = -\tfrac{1}{4} c^4 \frac{d}{d\beta}\left(\frac{e\beta}{\sinh\beta}\right) = \tfrac{1}{4} b^2 c^2,$$

$$c^4 \sum_1^\infty n^2 e^{-2n\beta} = \tfrac{1}{8} c^4 \frac{d^2}{d\beta^2}\left(\frac{e\beta}{\sinh\beta}\right) = \tfrac{1}{4} b^2 c^2 \coth\beta.$$

Using these results we can re-write (19) as

$$c^2 \iint \left(x\frac{\partial\psi_2}{\partial x} + y\frac{\partial\psi_2}{\partial y}\right) dxdy$$

$$= 2\pi(b^4\coth\beta - a^4\coth\alpha) + 2\pi c(b^2-a^2)y$$

$$- 4\pi c^2 k^2 \sum_1^\infty \frac{n^2 e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)} - 4\pi c^2 k^2 (\coth\alpha + \coth\beta) \times$$

$$\times \sum_1^\infty \frac{n\, e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)},$$

k, as we have already assumed, being the distance between the centres of the two circles.

Also

$$\iint y(x^2+y^2)\,dx\,dy = \pi c^2 \bar{y}(b^2-a^2)$$

$$+ 2c\pi(b^4\coth\beta - a^4\coth\alpha).$$

Substituting the results obtained above in (17.2) we get

$$-\frac{\mu\pi\tau}{W}\left[\tfrac{1}{2}(b^4-a^4) + 4c^2k^2\sum_1^\infty \frac{n\, e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)}\right]$$

$$= \bar{y} + \tfrac{1}{2}\mu\pi\frac{\sigma\bar{y}}{EI}(b^4-a^4) - \frac{\mu\pi c}{EI}(\tfrac{1}{2}+\sigma)(b^4\coth\beta - a^4\coth\alpha)$$

$$+ 2\mu\pi\frac{c^3k^2}{EI}\sum_1^\infty \frac{n^2 e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)}$$

$$+ 2\mu\pi\frac{c^2k^2}{EI}[c(\coth\alpha+\coth\beta) + 2\sigma\bar{y}]\sum_1^\infty \frac{n\, e^{-n(\alpha+\beta)}}{\sinh n(\beta-\alpha)}, \quad \ldots (20)$$

which determines τ. The infinite series in (20) are quite rapidly convergent.

(2) *Axis of symmetry in the plane of loading—*

The components of displacement and stress are now given by

$$u = \frac{\sigma W}{EI} x (l - z) (y - \bar{y}), \quad .. \quad .. \quad .. \quad .. \quad (21.1)$$

$$v = \frac{W}{EI} [\tfrac{1}{2} \sigma (l - z) \{(y - \bar{y})^2 - x^2\} + \tfrac{1}{2} lz^2 - \tfrac{1}{6} z^3] + \beta_1 z + \alpha_1, \quad (21.2)$$

$$w = \frac{W}{EI} [\chi (x, y) - (y - \bar{y}) (x^2 + lz - \tfrac{1}{2} z^2)] - \beta_1 y + \gamma_1, \quad (21.3)$$

$$\widehat{xz} = \frac{\mu W}{EI} \left[\frac{\partial \chi}{\partial x} - (2 + \sigma) x (y - \bar{y})\right] \quad .. \quad .. \quad .. \quad (22.1)$$

$$\widehat{yz} = \frac{\mu W}{EI} \left[\frac{\partial \chi}{\partial y} - (1 - \tfrac{1}{2} \sigma) x^2 - \tfrac{1}{2} \sigma (y - \bar{y})^2\right], \quad .. \quad (22.2)$$

$$\widehat{zz} = -\frac{W}{EI} (l - z) (y - \bar{y}), \quad .. \quad .. \quad .. \quad .. \quad (22.3)$$

$$\widehat{xx} = \widehat{yy} = \widehat{xy} = 0, \quad .. \quad .. \quad .. \quad .. \quad (22.4)$$

I being the moment of inertia of the section about an axis through G parallel to the x-axis.

Proceeding as in case (1) we find that the boundary condition (5) gives

$$\frac{\partial \psi_1}{\partial \xi} = 2 \sigma xy \frac{\partial y}{\partial \xi} - 2 (1 + \sigma) x\bar{y} \frac{\partial y}{\partial \xi} - y^2 \frac{\partial x}{\partial \xi}, \quad .. \quad .. \quad (23)$$

where

$$\chi = \tfrac{1}{2} \sigma \bar{y}^2 y + \tfrac{1}{2} \sigma \bar{y} (x^2 - y^2) + (1 - \tfrac{1}{2} \sigma) (x^2 y - \tfrac{1}{3} y^3) + \chi_1,$$

and ψ_1, is the function conjugate to χ_1.

A little calculation gives

$$\int x \frac{\partial y}{\partial \xi} d\xi = c^2 \sinh \eta \int \frac{\sin^2 \xi \, d\xi}{(\cos \xi + \cosh \eta)^3}$$

$$= \tfrac{1}{2} c^2 \sinh \eta \left[\frac{\sin \xi}{(\cos \xi + \cosh \eta)^2} - \int \frac{d\xi}{\cos \xi + \cosh \eta} + \cosh \eta \int \frac{d\xi}{(\cos \xi + \cosh \eta)^2}\right],$$

$$\int x y \frac{\partial y}{\partial \xi} d\xi = \tfrac{1}{3} c^3 \sinh^2 \eta \left[\frac{\sin \xi}{(\cos \xi + \cosh \eta)^3} - \int \frac{d\xi}{(\cos \xi + \cosh \eta)^2} + \cos \eta \int \frac{d\xi}{(\cos \xi + \cosh \eta)^3}\right]$$

and

$$\int y^2 \frac{\partial x}{\partial \xi} d\xi = x y^2 - 2 \int xy \frac{\partial y}{\partial \xi} d\xi.$$

Hence we can write

$$2\sigma \int xy \frac{\partial y}{\partial \xi} d\xi - 2(1+\sigma)\bar{y} \int x \frac{\partial y}{\partial \xi} d\xi - \int y^2 \frac{\partial x}{\partial \xi} d\xi$$
$$= 2(1+\sigma)[\tfrac{1}{3} x y^2 - \tfrac{1}{3} c^3 \sinh^2\eta \, H_2 + \tfrac{1}{3} c^3 \sinh^2\eta \cosh\eta \, H_3]$$
$$- xy^2 - 2(1+\sigma)\bar{y}[\tfrac{1}{2} xy - \tfrac{1}{2} c^2 \sinh\eta \, H_1$$
$$+ \tfrac{1}{2} c^2 \sinh\eta \cosh\eta \, H_2] \quad .. \quad .. \quad .. \quad (24)$$

where

$$H_r = \int \frac{d\xi}{(\cos\xi + \cosh\eta)^r}, \qquad (r = 1, 2, 3).$$

Putting

$$\psi_1 = -(1+\sigma)\bar{y} xy + \psi_2$$

and comparing (24) with (23) we see that the boundary condition can be written as

$$\psi_2 = c^2(1+\sigma)\bar{y} \sinh\eta \, H_1$$
$$- c^2(1+\sigma)\sinh\eta(\bar{y}\cosh\eta + \tfrac{2}{3} c \sinh\eta) H_2$$
$$+ \tfrac{2}{3} c^3(1+\sigma)\sinh^2\eta \cosh\eta \, H_3$$
$$- \tfrac{1}{3} c^3(1-2\sigma) \frac{\sin\xi \sinh^2\eta}{(\cos\xi + \cosh\eta)^3} + f(\eta) \quad .. \quad .. \quad (25)$$

where $f(\eta)$ is as yet an undetermined function of η.

To satisfy (25) we assume series of the form

$$S_r = \sum_{n=1}^{\infty} [C_{n,r} \sinh n(\eta - \alpha) + D_{n,r} \sinh n(\beta - \eta)] \sin n\xi,$$

$$(r = 1, 2, 3, 4). \quad .. \quad .. \quad .. \quad .. \quad (26)$$

Since H_1, H_2, H_3, $\sin\xi/(\cos\xi + \cosh\eta)^3$ are all odd in ξ we easily see that $f(\eta) = 0$.

$$(S_1)_{\eta=\alpha,\beta} = (\sinh\eta \, H_1)_{\eta=\alpha,\beta},$$

and proceeding as in (12) and (13) we find

$$C_{n,1} = \frac{(-1)^n 2 (e^{-n\beta} - 1)}{n \sinh n(\beta - \alpha)}, \quad D_{n,1} = \frac{(-1)^n 2 (e^{-n\alpha} - 1)}{n \sinh n(\beta - \alpha)} \quad .. \quad (27.1)$$

Again we have

$$(S_2)_{\eta=\alpha,\beta} = [\sinh\eta(\bar{y}\cosh\eta + \tfrac{2}{3} c \sinh\eta) H_2]_{\eta=\alpha,\beta},$$

$$(S_3)_{\eta=\alpha,\beta} = [\sinh^2\eta \cosh\eta \, H_3]_{\eta=\alpha,\beta},$$

$$(S_4)_{\eta=\alpha,\beta} = \left[\frac{\sinh^2\eta \sin\xi}{(\cos\xi + \cosh\eta)^3}\right]_{\eta=\alpha,\beta},$$

which give

$$C_{n,2} = \frac{(-1)^n 2(\bar{y}\cosh\beta + \frac{3}{2}c\sinh\beta)}{n\sinh^2\beta\sinh n(\beta-\alpha)}[e^{-n\beta}(n\sinh\beta+\cosh\beta) - \cosh\beta], \quad .. \quad .. \quad .. \quad .. \quad .. \quad (27.2)$$

$$D_{n,2} = \frac{(-1)^n 2(\bar{y}\cosh\alpha + \frac{3}{2}c\sinh\alpha)}{n\sinh^2\alpha\sinh n(\beta-\alpha)}[e^{-n\alpha}(n\sinh\alpha+\cosh\alpha) - \cosh\alpha] \quad .. \quad .. \quad .. \quad .. \quad .. \quad (27.3)$$

$$C_{n,3} = \frac{(-1)^n\cosh\beta}{n\sinh^3\beta\sinh n(\beta-\alpha)}[e^{-n\beta}(n^2\sinh^2\beta + \tfrac{3}{2}n\sinh 2\beta + 3\cosh^2\beta - \sinh^2\beta) - (3\cosh^2\beta - \sinh^2\beta)] \quad .. \quad (27.4)$$

$$D_{n,3} = \frac{(-1)^n\cosh\alpha}{n\sinh^3\alpha\sinh n(\beta-\alpha)}[e^{-n\alpha}(n^2\sinh^2\alpha + \tfrac{3}{2}n\sinh 2\alpha + 3\cosh^2\alpha - \sinh^2\alpha) - (3\cosh^2\alpha - \sinh^2\alpha)], \quad .. \quad (27.5)$$

$$C_{n,4} = \frac{(-1)^{n+1}n e^{-n\beta}}{\sinh\beta\sinh n(\beta-\alpha)}(n\sinh\beta+\cosh\beta) \quad .. \quad (27.6)$$

$$D_{n,4} = \frac{(-1)^{n+1}n e^{-n\alpha}}{\sinh\alpha\sinh n(\beta-\alpha)}(n\sinh\alpha+\cosh\alpha) \quad .. \quad (27.7)$$

Thus we can write

$$\psi_2 = c^2(1+\sigma)\bar{y}S_1 - c^2(1+\sigma)S_2 + \tfrac{3}{2}c^3(1+\sigma)S_3 - \tfrac{1}{2}(1-2\sigma)c^3 S_4,$$

and hence

$$\chi = \tfrac{1}{2}\sigma\bar{y}^2 y - \tfrac{1}{2}\bar{y}(x^2-y^2) + (1-\tfrac{1}{2}\sigma)(x^2 y - \tfrac{1}{3}y^3) - c^2(1+\sigma)\sum_{n=1}^{\infty}[\bar{y}C_{n,1} - C_{n,2} + \tfrac{3}{2}cC_{n,3} - \tfrac{1}{2}cC_{n,4}(1-2\sigma)/(1+\sigma)]\cos n\xi\cosh n(\eta-\alpha) + c^2(1+\sigma)\sum_{n=1}^{\infty}[\bar{y}D_{n,1} - D_{n,2} + \tfrac{3}{2}cD_{n,3} - \tfrac{1}{2}cD_{n,4}(1-2\sigma)/(1+\sigma)]\cos n\xi\cosh n(\beta-\eta),$$

where C's and D's are known from (27).

The convergency of the series S_1, S_2, S_3, S_4 can be proved in the same manner as in case (1).

Determination of a_1, β_1, γ_1.

Case (1)—

Instead of following Saint-Venant's mode of fixing a small area enclosing the centre of gravity of the section we take the more practical case of fixing two points on the axis of symmetry which is the y-axis in the present case.

If y_1, y_2 are the y-co-ordinates of the points to be fixed, we have the conditions

$$u = v = w = 0,$$

both when $x = z = 0, y = y_1$, and $x = z = 0, y = y_2$.

From (3) we have

$$\alpha_1 = \frac{\sigma l W}{2 EI}(y - \bar{y})^2, \qquad \gamma_1 = -\frac{W\chi_0}{EI},$$

where χ_0 is the value of χ at $x = 0$. It is easily seen that $\chi_0 = 0$ for all values of y. Hence $\gamma_1 = 0$. The first equation now shews that y_1, y_2 must satisfy the relation

$$y_1 + y_2 = 2\bar{y}.$$

Hence we can fix any two points on opposite sides of the centre of gravity of the section such that the sum of their y-co-ordinates is equal to $2\bar{y}$. For example, if we fix the centre of the outer circle, then $y_1 = b \cosh \beta$, and $y_2 = -b \cosh \beta + 2(b^2 \cosh \beta - a^2 \cosh \alpha)/(b^2 - a^2)$.

Case (2)—

In this case, too, we can fix two points on the axis of symmetry. The condition is

$$u = v = w = 0$$

at these two points give

$$\alpha_1 = -\frac{\sigma l W}{2 EI}(y - \bar{y})^2, \qquad \gamma_1 = \beta_1 y - \frac{\chi_0 W}{EI}$$

The first shews that

$$y_1 + y_2 = 2\bar{y}.$$

Putting $y = y_1$ and $y = y_2$ in the second we get two equations to determine the two unknown constants β_1 and γ_1.

It appears, therefore, that we can always fix two points on the axis of symmetry of the section of a cylinder possessing uniaxial symmetry. These points lie on opposite sides of the centre of gravity of the section and are such that

$$y_1 + y_2 = 2\bar{y},$$

y_1, y_2 being their y-co-ordinates, and $\bar{y}$ that of the centre of gravity, *the load acting in any direction whatever.*

In Part II we shall obtain numerical results for the amount of twist produced in the asymmetrical case and for the value of stress at different points of the section.

MAGNETIC ANISOTROPY OF NATURALLY OCCURRING SUBSTANCES.

II. Molluscan Shells.

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1. *Introduction.*

In a previous communication,[1] the author has described how the determination of the magnetic anisotropy of the nacre of iridescent shells enables us to gain information regarding its inner architecture. The results also seemed to indicate that the cementing medium conchyolin itself has most probably got a quasi-crystalline structure. The method thus proved itself to be fruitful, and in the present investigation it has been extended to a more general study of the structure of molluscan shells.[2] These have been extensively studied by means of the polarising microscope and the contributions of W. J. Schmidt[3] and O. Boggild are of special interest. While Schmidt confined himself to a detailed examination of some typical shells of the various classes of molluscs, O. Boggild has made an exhaustive and systematic study of them. The present work is concerned with the shells of *Placuna placenta, Pinna bicolor, Meretrix casta, Mactra lurida, Mactra hebbalensis, Vulsella rugosa* and *Turbinella pirum* (Indian *Chank*). A minute structural examination of these shells bringing out all the peculiarities of arrangement and constitution of the elementary crystals is not possible by the magnetic method. But the presence of magnetic anisotropy can definitely establish the crystalline character of the elements that go to build up the shell, as well as give a general indication of the most probable orientations ; and in some favourable cases such as *Placuna placenta*, it is possible to get significant information concerning the elementary crystals themselves, as will be shown later.

2. *Description of the Shells.*

Placuna placenta is the well-known species of window-pane oyster found in the Indian Ocean. The shell has got a pearly lustre, is faintly iridescent, and consists exclusively of calcite. It cleaves into thin leaves like mica, and the structure has been described by Boggild as foliated. When examined

under the microscope numerous fine lines (*streifen*) can be seen on the foliæ, parallel to one another the surface resembling a fibre mat. The leaves easily break into small strips in the direction of these lines. By examination under the polarising microscope, W. J. Schmidt has found that the thin laminæ show extinction in the direction of the fine lines. Conoscopically examined, they always gave a negative uniaxial eccentric interference pattern. This indicates that the optical axes of the elementary crystals are inclined to the plane of the laminæ. Schmidt has also found that the smallest elements of the shell are extremely thin leaf-like structures, about 1μ thick, 5μ wide and 100μ long. They are arranged with their lengths parallel to the fine lines on the laminæ. Their accurate crystallographic determination was not, however, found to be possible. Boggild also has mentioned the inclination of the optic axes of the crystals to the laminar plane.

The shell of *Pinna bicolor* consists of two layers, an upper prismatic calcitic layer, and a lower aragonite nacreous one. The nacreous layer, which shows bright iridescent colours, can be easily chipped off and is usually very thin. Schmidt has isolated the tiny prisms of calcite in the upper layer and has found that the optic axis coincides with the prism axis. Each prism is a single crystal of calcite arranged in the shell with its axis normal to the shell surface. It has also been found that there is very little difference between the different species of *Pinna*.

The common feature of the shells of the *Mactra* sp., according to Boggild, is the crossed lamellar concentrical layer. This is however in many cases irregular. *Mactra lurida* is a white aragonite shell with a violet coloured patch in the middle. The lowest porcellanous layer was taken for examination from both the white as well as the coloured portions. The shell of *Mactra hebbalensis* is dark in colour and very brittle.

Vulsella rugosa has got a very thin and fragile shell. It consists of an upper prismatic calcitic layer and an extremely thin nacreous layer below. The shell of *Meretrix casta* is hard and porcellanous in appearance. The "*Chank*" is very well known in South India.[5] The shell is white and chalky in appearance and consists of several calcitic layers. These were found to break easily along a particular direction in a somewhat similar manner as the cleaving of crystals. Only the lowest layer, which appeared to be translucent, was taken up for examination.

3. *Magnetic Anisotropy of Calcitic Shells.*

It is convenient from the experimental standpoint, to determine the anisotropy of the shells, firstly in the plane of the shell layer, and then in the two perpendicular planes determined by the directions of maximum and

minimum susceptibility in the shell plane. In the case of the nacreous layer, where we have got a normal orientation of the aragonite crystals, the orientations could be deduced from the results in a simple and straightforward manner. But when inclined orientation of the crystals is present, as in the calcitic shell, *Placuna placenta*, the orientations may be deduced from the following considerations.

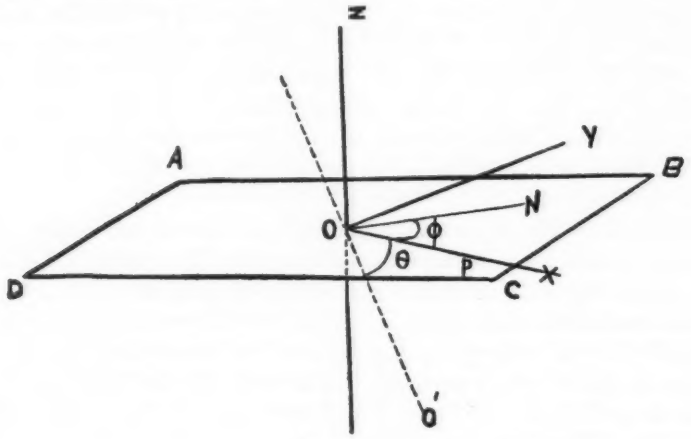

FIG. 1.

Let ABCD (Fig. 1) represent the plane of the folia and let OO′ be the direction of the trigonal axis of the calcite crystals inclined at an angle to the plane—Let a rectangular co-ordinate system be chosen such that the direction of the projection of OO′ on the plane is the X-axis. OY in the plane represents the Y-axis. If K_1 and K_2 are the magnetic susceptibilities along and perpendicular to the trigonal axis respectively and if ON is any arbitrary direction in the plane making an angle θ with OX,

$$\chi_{ON} = K_1 \cos^2\theta \cos^2\phi + K_2 (\sin^2\theta \cos^2\phi + \sin^2\phi)$$

$$\frac{d\chi}{d\phi} = (K_2 - K_1) \sin 2\phi \cos^2\theta.$$

This will be zero when $\phi = 0$ or $90°$.

χ is maximum when $\phi = 0$

and equals $\chi_1 = K_1 \cos^2\theta + K_2 \sin^2\theta$.

The minimum value of $\chi = \chi_2 = K_2$

when $\phi = 90°$.

OX and OY are thus the directions of maximum and minimum diamagnetic susceptibility in the plane. The magnetic anisotropy

$$\Delta\chi = (K_1 - K_2) \cos^2\theta.$$

The directions OX and OY can be easily located by suspending the shell with the plane horizontal in a uniform magnetic field and observing the orientation. When the piece of shell is suspended with the OX direction vertical, the orientation will be with the plane parallel to the field.

and $\Delta\chi = (K_1 - K_2) \sin^2 \theta$.

When, however, it is suspended with the OY direction vertical, the plane will make an angle $(90° - \theta)$ with the field.

Hence, θ can be known.

and $\Delta\chi$ will be $= (K_1 - K_2)$.

4. *Experimental.*

Both Krishnan's[6] oscillation as well as torsional methods were employed, for the determination of anisotropy according to convenience. The oscillation method has already been described in the previous communication by the author. Here, the torsional method will be briefly described.

The chief advantage of this method is that very small pieces can be employed for examination, and this is desirable in the case of shells for obvious reasons. The principle of the method is as follows :—If an anisotropic body is freely suspended in a uniform magnetic field, it will orientate itself such that the directions of maximum and minimum (algebraic) susceptibility in the plane of oscillation about the axis of suspension, will be along and perpendicular to the field respectively. If the torsion of the fibre is zero in this position, and if the torsion-head is turned slowly until at a critical point the body swings round suddenly, then the anisotropy in the plane is given by

$$\Delta\chi = \frac{2(\alpha_c - 45°)\pi}{180°} \cdot \frac{c}{mH^2}$$

where

α_c = The angle through which the torsion-head has been turned.
c = modulus of torsion of the fibre.
m = Mass of the body.
H = Field strength.

At the critical position the body will make an angle of 45° with its initial position. However, in the case of some of the shells it was observed that this angle was considerably greater. This may be attributed to the presence of an irregularity in the orientation of the crystals which, so to speak, blunts the critical point. The oscillation method also was tried in such cases to check up.

The anisotropy was determined as usual, for three modes of suspension ; firstly, with the plane horizontal—from the orientation the directions of maximum and minimum susceptibility in the plane are known ; then with these directions vertical respectively.

TABLE I.

$\chi_1' > \chi_2' > \chi_3'$ *Algebraically.*

Shell	Class	Mode of suspension	Orientation	Specific anisotropy × 10^8 E.M.U.	Remarks
Placuna placenta ..	Bivalve	(A) Plane of the shell folia horizontal	Direction of the fine lines $\perp^r$ to the field	$\chi_1'-\chi_2'=0{\cdot}8$	The optic axes of the crystals make an angle of 64° with the laminar plane and are inclined in the direction of the fine *streifen*
		(B) χ_1' axis vertical	Plane made an angle of 26° with the field	$\chi_2'-\chi_3'=5{\cdot}2$	
		(C) χ_2' ,,	Plane $\parallel^l$ to the field	$\chi_1'-\chi_3'=4{\cdot}6$	
Pinna bicolor (calcitic layer)	,,	(A)	Indefinite	$0{\cdot}0_6$	optic axis $\perp^r$ to the shell plane
		(B) ,,	Plane $\parallel^l$ to the field	,, $5{\cdot}6$	
		(C)	,,	$5{\cdot}8$	
Pinna bicolor (nacreous layer) ..		(A)	Line of growth $\parallel^l$ to the field	$0{\cdot}3$	*c* axes of the aragonite crystals normal to the laminar plane. *a* axes probably $\perp^r$ to the line growth
		(B) ,,	Plane $\parallel^l$ to the field	,, $7{\cdot}0$	
		(C)	,,	$7{\cdot}2$	
Meretrix casta ..	,,	(A)	..	$0{\cdot}0_5$	Trigonal axis of the crystallites of calcite $\perp^r$ to the shell plane
		(B) ,,	Plane $\parallel^l$ to the field	,, $5{\cdot}7$	
		(C)	,,	$5{\cdot}8$	
Mactra lurida ..		(A)	..	$0{\cdot}0_7$	Trigonal axis of the crystallites $\perp^r$ to the plane
		(B) ,,	Plane nearly $\parallel^l$ to the field	,, $5{\cdot}7$	
		(C)	,,	$5{\cdot}7$	
Mactra hebbalensis ..	,,	(A)	Line of growth nearly $\parallel^l$ to the field	$1{\cdot}7$	The values obtained with different specimens differed considerably. Those given are only approximate
		(B) ,,	Plane made an angle of about 15° with field	,, $6{\cdot}2$	
		(C)	Plane nearly parallel to the field	$5{\cdot}0$	

Vulsella rugosa (nacreous layer) ..	„	(A)	..		0·1	The cokes of the aragonite crystals normal to the laminar plane
		(B)	„	Plane parallel to the field	„ 7·2	
		(C)		„	7·4	
Vulsella rugosa (calcitic layer) ..		(A)	..		0·1	Trigonal axis of the crystals ⊥r to the shell plane.
		(B)	„	Plane parallel to the field	„ 6·2	
		(C)		„	6·4	
Turbinella pirum ..	Gastropod	(A)		Line of cleavage ∥r to the field ..	0·4	Here also the values for different specimens differed by more than 15% and the orientation by about 10°
		(B)	„	Plane made an angle of about 20° with field ..	„ 5·3	
		(C)		Plane nearly parallel to the field ..	4·7	

TABLE II.

	Mode of suspension	Orientation	Specific anisotropy $\times 10^8$ E.M.U.
Calcite	Trigonal axis horizontal	Trigonal axis normal to the field	4·0

For each mode of suspension, there are however two ways of suspending the piece ; the second being with the shell piece turned upside down. This gives an accurate method of determining the orientation in the field. We have only to take the mean of the two orientations of the piece corresponding to the two ways of suspending it.

In the author's earlier communication, it was mentioned that for determining the modulus of torsion of the fibre, a rectangular glass plate was employed. This cannot give accurate values, and therefore here, a circular disc suspended at its centre with its plane horizontal, was used. The field strength was determined with the help of the Grassot Fluxmeter. The other experimental details have been described in the earlier paper of the author.

The results are entered in Table I. Table II gives the values for a single crystal of calcite. In the notation adopted χ_1' and χ_2' are the maximum and minimum susceptibilities in the plane of the shell (algebraically) along mutually perpendicular directions. χ_3' is that normal to the plane of the shell.

The shells were all found to be diamagnetic.

5. *Discussion.*

It is easily evident from the results that the shell elements are crystalline, and regularly arranged to a greater or less extent.

In the case of *Placuna placenta* significant conclusions can be drawn since consistent results were obtained with several specimens. The behaviour of the shell in a uniform magnetic field corresponds exactly with the case dealt with theoretically, thereby indicating inclined orientation of the trigonal axes of the calcite crystals to the shell plane. The optical axis of the small crystals are inclined to the laminar plane at an angle of 64° and the inclination is in the direction of the fine lines seen on the thin foliæ. A simple calculation shows that the trigonal axis in a single crystal of calcite makes almost the same angle (63°, 48′) with faces of the form {110}. This evidently means that the long leaf-like elementary crystals of calcite have the direction of a crystal axis (which may be denoted the a_3-axis) lying along their lengths, the (110) planes being parallel to the laminar plane. These crystals themselves are arranged with their lengths parallel to the direction of the fine lines on the foliæ.

It is very likely, in view of the extreme thinness of the elements, that the (110) and $(\bar{1}\bar{1}0)$ faces are well-developed in them and this peculiar crystal *habit* then accounts for the foliated structure of the shell also.

We know that the prisms of calcite are orientated in the upper layer of *Pinna* with the prism axis normal to the shell surface. The anisotropy determinations show that the trigonal axes of the crystals are normal to the shell surface : which means that the optical axes of the prisms coincide with the prism axes. This agrees with the observations of Boggild. In the nacreous layer it is seen that the *c*-axes of the aragonite crystals are orientated normal to the laminar plane. As regards the orientation of the *a*- and *b*-axes, one cannot speak with certainty in view of the complications already discussed in the earlier communication of the author. It may, however, be tentatively inferred that the *a*-axes of the crystals are probably orientated perpendicular to the line of growth.

With *Mactra hebbalensis* no consistent results could be obtained. This is most probably due to considerable irregularity of structure. The *c*-axes of the aragonite crystals in this case seem to be inclined to the shell surface. In *Mactra lurida*, the probable orientation of the aragonite crystals is with the *c*-axes normal to the shell surface. No great difference was found in the anisotropies of the white and coloured portions of this shell.

In the calcitic layers of the shells of *Meretrix casta* and *Vulsella rugosa*, the crystals are evidently orientated with the optical axes more or less normal to the shell plane. In *Chank*, however, an inclined orientation is present.

It may be noted that in the case of the calcitic layers of all the shells investigated the values of the magnetic anisotropy are nearly the same as that of calcite. But in view of the irregularity in the arrangement of the crystals which we should expect, the values ought to be lower, but actually they are some 20% higher. The reason is not quite clear. It is probable that here also, the cementing medium makes a contribution to the anisotropy due to a quasi-crystalline structure as suggested in a previous communication by the author. Further investigation is necessary to elucidate this point. The magnetic anisotropy of the nacre of *Vulsella rugosa* and *Pinna bicolor* is seen to be higher than that of the respective calcitic layers below. This is evidently due to the greater regularity of arrangement of the crystallites in the former in layers, a characteristic feature of all nacre.

In conclusion, the author wishes to express his thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for the kind interest shown during the progress of the work, and for helpful suggestions and criticism.

Summary.

The magnetic anisotropy of the shells of *Placuna placenta*, *Pinna bicolor*, *Meretrix casta*, *Vulsella rugosa*, *Mactra* sp., and *Turbinella perium*, have been determined. In all cases, the crystalline character of the elements as

well as their regularity of arrangement have been established and the probable orientations deduced. In the case of *Placuna placenta* information regarding the character and *habit* of the crystalline elements has been obtained.

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ON FERMI'S THEORY OF β-DECAY.

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The introduction of the factor

$$\frac{\nu^2 \Delta \nu}{\pi^2 c^3}, \tag{1}$$

the number of oscillators per unit volume within the frequency interval $\Delta\nu$ for both neutrino and electron waves in Fermi's theory of the β-decay[1], seems to require some closer investigation. As in the treatment of analogous problems in the theory of radiation, the result of the integration, after multiplication by (1), over the whole frequency range of the neutrino waves is determined by a resonance term; the integration over all possible electron frequencies gives rise to a factor of the order of magnitude of the total number of oscillators contained in the frequency interval from 0 to ν_0, the maximum frequency of the electrons emitted,[2]

$$\frac{\nu_0^3}{\pi^2 c^3} \tag{2}$$

Since an electron is emitted with a definite energy, and since the total transition probability is the average of the transition probabilities for the electrons of different energies, the appearance of a factor of the order of magnitude of the total number of oscillator seems to be somewhat surprising. We should rather expect a much smaller numerical factor to appear in the final result, corresponding to the average number of oscillators actually interacting with the electrons, having different, but definite, energies.

To make this point clear, let us consider Planck's derivation of (1). The energy of an oscillator of characteristic frequency ν_0 in interaction with radiation of the frequency ν is

$$T(\nu) = \frac{e^2 \overline{E_\nu^2}}{8m} \frac{1}{(\nu_0 - \nu)^2 + \gamma^2} \tag{3}$$

Remembering that $\gamma = \frac{1}{3} \frac{e^2 \nu^2}{mc^3}$, and further that the density of radiation with frequencies in the interval $\Delta\nu$

$$\rho_\nu = \frac{3 \overline{E_\nu^2}}{8\pi} = U_\nu \Delta\nu,$$

we obtain on integration the average oscillator energy

$$T_\nu = \frac{\pi^2 c^3}{\nu^2} U_\nu = \rho_\nu \cdot \frac{\pi^2 c^3}{\nu^2 \Delta\nu} \tag{4}$$

Hence follows (1) as the ratio $\frac{\rho_\nu}{T_\nu}$.

In the case of interaction of an oscillator with monochromatic radiation, having its own characteristic frequency, we obtain in a similar way

$$T_\nu = \rho_\nu \cdot \frac{c^3}{\nu^2} \frac{\pi}{\gamma}, \tag{5}$$

and therefore

$$\frac{\rho_\nu}{T_\nu} = \frac{\nu^2 \gamma}{\pi c^3} \tag{6}$$

This expression becomes identical with (1), if

$$\Delta\nu = \pi \gamma \tag{7}$$

We might have expected a result like this, for 2γ is the so-called natural line width. We obtain of course the same transition probability for the interaction with both "white" and monochromatic radiation, but the same is not necessarily the case for multiple processes.

In case of interaction of light quanta and electrons we have for simple processes

$$\gamma \sim \alpha^3 \nu, \tag{8}$$

α being the fine structure constant.[3] Subtituting this expression in (6), we get

$$\frac{\rho_\nu}{T_\nu} \sim \frac{1}{\pi}\left(\frac{\nu \alpha}{c}\right)^3 \tag{9}$$

In the theory of β-decay the process of emission of every electron independently may have to be treated in a similar way. Let us assume that (8) is applicable to β-radiation also. This conjecture does not seem to be entirely unfounded, since the assumption implied in (8) that the wave-length of the radiation emitted or absorbed is much greater than the dimensions of the system of particles concerned, is also valid for β-radiation, and since, further, (8) does not depend upon the mass of the particles. Fermi's expression for the transition probability has then to be multiplied by a factor of the order of magnitude α^3, and hence a different value for the constant g in Fermi's interaction formula is obtained. As the transition probability is proportional to g^2, we get

$$g^2 \sim \alpha^{-3} g_F^2 \tag{10}$$

$g_F \sim 4 \cdot 10^{-50}$ gr. cm.^{5} sec.$^{-2}$. being Fermi's original constant, and thus

$$g \sim 6 \cdot 10^{-47} \text{ gr. cm.}^5 \text{ sec.}^{-2} \tag{10'}$$

While the order of magnitude of Fermi's g_F, when applied to the problems of shower production and the interaction of heavy particles, appeared to be too small, this is no longer the case with the value (10).

Let us first consider the interaction of heavy particles. In this problem no integrations like those discussed above are involved. Except for the larger value for the constant g, Iwanenko's results[2] remain thus valid. He derived the following expression for the interaction energy

$$|V| = \hbar c \cdot \frac{(g/\hbar c)^2 (\hbar/m c)^{2(m+n)} \cdot (2m + 2n + 2)!}{\pi^3 (2r)^{2m+2n+5}} \tag{11}$$

m and n being the order of the derivatives of the characteristic functions of the neutrino and electron waves respectively, introduced in Fermi's interaction formula. This expression can be written in a very simple form. Using (10') we obtain $g/\hbar c \sim 2 \cdot 10^{-30}$ cm.^{2}, while $\alpha e^2/mc^2 \sim 4,1 \cdot 10^{-30}$ cm.^{2} Thus we see that

$$\frac{g}{\hbar c} \sim \tfrac{1}{2} \left(\alpha \frac{e^2}{m c^2} \right)^2 \tag{12}$$

Introducing further $2r = \rho . e^2/mc^2$ ($e^2/mc^2 = 2{,}80 \cdot 10^{-13}$ cm.), where ρ is a numerical factor, which will not differ considerably from unity, we obtain

$$|V| \sim m c^2 \frac{\alpha^{-2(m+n)+3}}{\rho^{2(m+n)+5}} \cdot \tfrac{1}{4} (2m + 2n + 2)! \tag{13}$$

It is apparent that V will be of the required order of magnitude, mc^2, for $2m + 2n \sim 3$, thus $m + n = 1$ or 2. With Fermi's value, (12) contains an additional factor α^3; therefore $2m + 2n \sim 6$ is required, and $m + n = 3$.

A similar result concerning $m + n$ is obtained on introducing the new value for g in the expression, which Heisenberg[4] obtained for the ratio of the energy of the electrons produced in showers and the energy of the proton,

$$\frac{E}{M c^2} \sim \frac{\hbar}{M c} \left[\frac{g}{\hbar c} \left(\frac{\hbar}{m c} \right)^{m+n} \right]^{-\frac{1}{2+m+n}} \tag{14}$$

Using Fermi's value g_F he calculated the numerical values for this ratio, which are compared with those obtained with g (10'), in the following table:

$m + n$	0	1	2	3
E/Mc^2 with g_F	580	5,7	0,31	0,14
E/Mc^2 with g	15	0,45	0,087	0,033

Heisenberg concluded that the result is reasonable only for $m + n = 2$ or 3. We see that with g (10') the ratio E/Mc^2 becomes of the same order of magnitude already for $m + n = 1$. Thus both problems considered seem to point to the same conclusion. It is remarkable that also Konopinski and Uhlenbeck[5] obtained the best agreement between the theoretical curves for the

intensity distribution of the β-ray spectra, derived with the help of a generalisation of Fermi's interaction formula, and those observed experimentally, for $m + n = 1$. The discrepancy between this result and Heisenberg's and Iwanenko's estimate, $m + n = 3$ (v.l.c.), would not arise under the assumptions made in this note.

Summary.

Planck's derivation of the formula for the number of oscillators per unit volume, together with the relation between the frequency and the natural line width, suggest that a factor of the order of magnitude α^{-3} may have to be introduced in Fermi's expression for the transition probability in the theory of β-decay. The new value for Fermi's constant g is such that we obtain satisfactory aggreement between Konopinski–Uhlenbeck's conclusions concerning the intensity distribution of β-ray spectra and the results of Heisenberg's and Iwanenko's application of Fermi's theory to the production of electron showers by cosmic rays and the interaction of heavy particles respectively.

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THE VISIBILITY OF ULTRASONIC WAVES IN LIQUIDS.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

Immediately after it was shown in 1932 that light is diffracted by high frequency sound waves, Hiedemann and his co-workers[1] at Köln demonstrated very clearly that ultrasonic waves travelling in a medium can be observed visually on viewing through a microscope. The field of view exhibits a number of equidistant bright sharp lines, especially when a monochromatic source of light is used. This method enables one to measure accurately the velocity of sound in a liquid from a knowledge of the distance between two fringes, which is equivalent to half the wave-length, λ*. It is easier to observe the stationary waves while for the progressive waves one has to use a Kerr cell.

Recently, on the basis of the Raman–Nath[2] theory for the propagation of light in a medium filled with sound waves, Pisharoty[3] worked out the visibility of ultrasonic waves, considering the amplitude and phase changes occurring in the transmitted beam. His theory predicts that the fringes repeat themselves after an interval depending on the wave-lengths of light and of sound for the case of progressive sound waves. Some minor errors in his paper have been corrected by Nath[4] and the latter's theory which is of a very general character, is in full agreement with the author's observations. Meanwhile a paper by O. Nomoto[5] has appeared giving the explanation of the visibility of ultrasonic waves in liquids, taking as the basis the Raman–Nath theory and arrives at the same results as Nath. He has also verified experimentally, the periodicity phenomenon, independently of the author.

Soon after Pisharoty's paper was published the author set up the experimental arrangement and verified the predicted periodicity effect. This result was reported by Raman and Nath in a letter to *Nature* (**138**, p. 616) and in a separate note by the author published in *Current Science* for September[6] almost all the expected results of the theory were confirmed.

The author has obtained some further interesting results in the intermediate positions between the intervals showing the periodicity phenomenon; namely in doubling, trebling and quadrupling of the fringes. These, together with the effect of supersonic amplitude on the fringes and the effect of obliquity on them are reported in this paper. Photographs of the sound field by the schlieren method are also given.

A simple explanation, due to Nath, for the periodic visibility of ultrasonic waves is appended.

2. *Results of Observations.*

With the same oscillator set as the one previously used by the author, and at a frequency of $7 \cdot 164 \times 10^6$ c./s. the standing waves were observed through a microscope, with a magnification of between 25 and 80 on different occasions. All the photographs of the waves were taken at a magnification roughly equal to 40.

The microscope could be moved easily in a direction parallel to that of light and the exact amount by which it has moved could also be read off on a scale attached to it, correct to one-tenth of a millimetre.

After setting the quartz piece in oscillation, the microscope was focussed on the sound wave grating at a position very near the face of the cell. It was slowly moved back, away from the cell when it was observed that the pattern had disappeared giving only a constant intensity grating. On still further moving the microscope, the pattern appeared but with double the number of fringes. A further small displacement produced two fringes in between the original pattern, with three fringes at a still slightly greater distance. Between this position and the next, at which the original pattern repeated, there appeared only a constant intensity grating. If we call the distance between the first position and its repetition, by d, then the above series of changes in the number of fringes of 2, 3 and 4 occurred respectively at $\frac{1}{2}\,d$, $\frac{2}{3}\,d$ and $\frac{3}{4}\,d$. These results are very significant as yet they are unexplained.

Fig. 1 in the plate gives the visibility of the waves at 0 (initial focus), $\frac{1}{2}\,d$, $\frac{2}{3}\,d$ and at d respectively, while the effect at $\frac{3}{4}\,d$ was observed but no clear photograph of it could be obtained. The last picture is seen to be a repetition of the first, while in the second, a fringe in between the original ones has appeared. In the third photograph, taken at $\frac{2}{3}\,d$, two fringes between the positions of the original fringes can be observed clearly. These are repeated at further distances. All the photographs were taken using 5461 Å of the mercury arc as the source.

The theory developed by Nath explains the periodicity of the phenomenon at distances of d. The theory also indicates multiplicity of the fringes under suitable experimental conditions.

These distances are given below, as measured in *m*-xylene at a frequency of $7{\cdot}164 \times 10^6$ c./s.

Liquid	Initial position	doubling at	Trebling at	Quadrupling at	Repeated at d
m-Xylene	0	15·6 mm.	20·8 mm.	23·4 mm.	31·1 mm.

This distance d corresponds to $\frac{\lambda^{*2}}{2\lambda}$ in the theory of Nath, λ^* and λ representing the wave-lengths of sound and of light respectively. It is therefore important to remember that if we know d and λ, it is possible to calculate λ^*, and hence v the ultrasonic velocity in the liquid concerned. This offers an easy and a fairly accurate method for the determination of ultrasonic velocity in liquids, in addition to the two already available, in this region of frequencies ; namely, (1) that due to diffraction of light by ultrasonic waves extensively used by the author ; and (2) the visibility effect, where from the distance between two fringes, and the magnification used of the microscope, the half wave-length of sound is determined.

Using this periodicity phenomenon, the sound velocities at $7{\cdot}164 \times 10^6$ c./s. have been determined in four liquids, just to illustrate the method. They are given below :—

Liquids	Sound velocity	Temp.
Benzene	1302 m./s.	25°C.
CCl_4	918 ,,	,,
m–Xylene	1320 ,,	,,
Anisol	1441 ,,	,,

The agreement between these values and those obtained by other methods is satisfactory.

3. Visibility of the Ultrasonic Waves at Different Intensities.

It would be worth while to examine whether or not, the sharpness of the fringes was observed at all supersonic intensities. Towards this, the

oscillator set was arranged to give the maximum intensity it could give and observing this pattern through the microscope, the amplitude was slowly decreased. It was noticed that the once well-defined sharp lines became blurred and wider, getting less intense at the same time. Finally at even less oscillatory current, the pattern could not be seen.

It should be remarked here, that the point of focus shifts for different amplitudes. It was noticed that for less supersonic intensity the focus shifted away from the cell, *i.e.*, towards the observer. Nonetheless, the distance d remained the same. This is explained on Nath's theory.

Fig. 2 gives two photographs taken at (*a*) higher and (*b*) lower supersonic intensity. The upper picture has sharp lines, while in the lower one, the bright spaces representing the fringes are as wide as the dark spaces. For the lower one the focus had shifted by 10·4 mm. towards the observer.

4. At Oblique Incidence.

It will be recalled that great asymmetry in the diffraction spectra produced by the passage of high frequency sound waves in a liquid persisted, when sound waves were inclined at a small angle to the beam of light. At greater angles of inclination the spectra tended to disappear. The effect of obliquity of the sound to light beam was studied in the microscopically visible fringes also and in a general way it may be remarked that asymmetry in the pattern was not observed. Instead, the fringes tended to lose their sharpness and to become wider, at the same time becoming less intense. Whether there was any asymmetry in the distribution of intensity in the fringes themselves could not be very clearly established ; but it should be said that if present, it was not marked to any noticeable extent.

At greater inclinations the fringes diasppeared altogether. In the experiment carried out with a crystal 20 mm. × 20 mm. × 2 mm. no fringes could be seen at 1° 14′ and over ; the frequency of vibration being 7·164 × 10^6 c./s. and the liquid *m*-xylene.

Fig. 3 gives two pictures, one at parallel incidence, and the other at an inclination of 53′ when the fringes were just visible. Beyond 1° 14′ the pattern was only a constant intensity grating.

5. Form of the Sound Field.

By an arrangement usually employed for obtaining schlieren photographs of sound waves, pictures were taken at various amplitudes of the sound wave and also those near the oscillating quartz and at a distance from it.

In order that the effect may be pronounced and well defined, just in front of the quartz piece and in contact with it, a piece of copper plate with a circular aperture of 2 mm. diameter was placed. The sound field was illuminated by a converging beam of light, coming to a focus just in front of a camera, which itself is focussed to the sound field in the liquid. By adjusting the oscillatory current, the amplitude of the sound wave could be altered and it was noticed that the form of the field changed much with supersonic intensity.

Fig. 4 gives a series of four photographs taken of the sound field at oscillatory current of (*a*) 150 mA, (*b*) 250 mA, (*c*) 400 mA and (*d*) 500 mA respectively. Figs. 4 (*a*) and 4 (*b*) show the sound fields separated from the oscillating quartz, but the form is quite the same as the one shown by Boyle at much lower frequency and recently by Grossmann and Hiedemann[7] and by Hiedemann[7] by quite different methods. The elongated oval shape is quite marked and characteristic. The photographs 4 (*c*) and 4 (*d*) at higher intensities reveal different patterns for the sound field and are in close contact with the quartz. These two are different from the earlier ones and also from each other. Subsidiary maxima, required by the older theory of diffraction at an aperture, are also visible.

Figs. 5 (*e*) and 5 (*f*) are two photographs with one face of the quartz quite open, without any aperture. It is seen that the sound field is almost compact very near the quartz, but slowly converges at a distance while much of the sound seems to get diffused as evidenced by a large number of streaks in 5 (*f*). Such diffusion of sound, outside the path, seems to be quite common as Figs. 4 (*c*) and 4 (*d*) also reveal.

The author has great pleasure in thanking Sir C. V. Raman for his interest in the work.

6. *Summary.*

The paper gives results on the visibility of ultrasonic waves in liquids. It is shown that the Hiedemann effect repeats at intervals of $d = \frac{\lambda^{*2}}{2\lambda}$ for standing waves, in agreement with the theory of Nath. Further, doubling, trebling and quadrupling have been observed at $\frac{1}{2}\,d$, $\frac{2}{3}\,d$ and $\frac{3}{4}\,d$. The effects of changes in supersonic intensity and obliquity on the microscopically visible fringes are observed and discussed. It is pointed out that while the theory gives broad bright lines, experimental results show very sharp lines. Photographs of the sound fields obtained by the schlieren method are also reproduced, and their characteristic forms discussed.

APPENDIX.

By N. S. Nagendra Nath.

A Simple Method of Deriving the Periodic Visibility of Ultrasonic Waves.

If a plane beam of light enters a rectangular cell containing ultrasonic waves travelling perpendicular to the direction of the incident light, the beam of light on the emergent face should be corrugated periodically in phase and amplitude with the period of the wave-length of ultrasonic waves along the direction of the propagation of those waves, for they create periodic fluctuations in the density of the medium and consequently in its optical properties. It is also easy to see that a periodic corrugated beam of light can be regarded as the superposition of a set of ordinary plane waves making characteristic angles with the direction of the incident light ($\sin \theta_n = n\lambda/\lambda^*$). If one considers the propagation of this set of plane waves in a ***homogeneous*** medium like air, it will also be easy to see that the propagation of any individual wave is independent of the others. But the form of the wave-front will not be the same everywhere in the homogeneous medium as the individual waves travel in different directions.

Let us, for simplicity, consider only two component waves, the 0th and the nth, as shown in Fig. 6. The superposition of these two waves at A will be the same as at B after a definite time during which time each of them travels a distance x, if the wave-front of the nth order passing through O′ is exactly in the same phase as the one which is at a distance x from the wave-front of the nth order passing through O. The above condition can

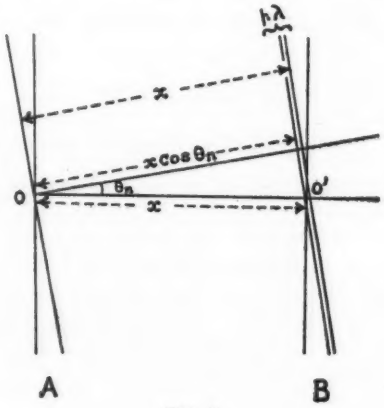


FIG. 6.

FIG. 1.

Periodicity phenomenon.

FIG. 2.

With change in supersonic intensity.

FIG. 3.

Obliquity phenomenon.

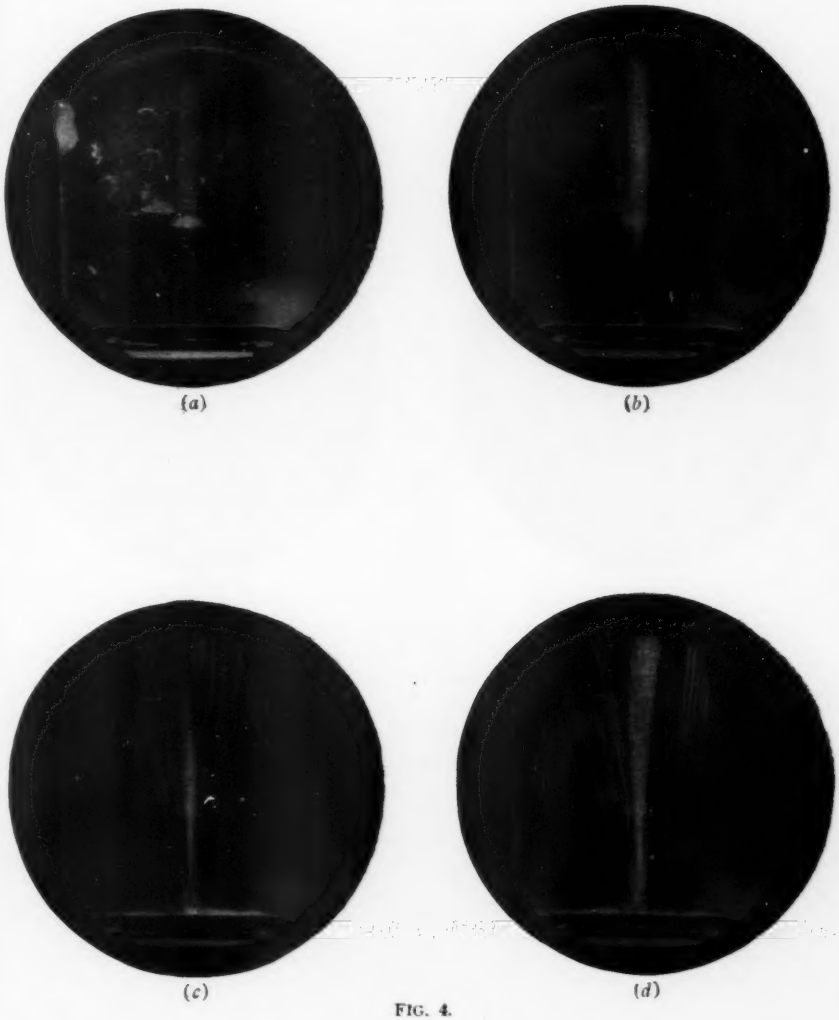
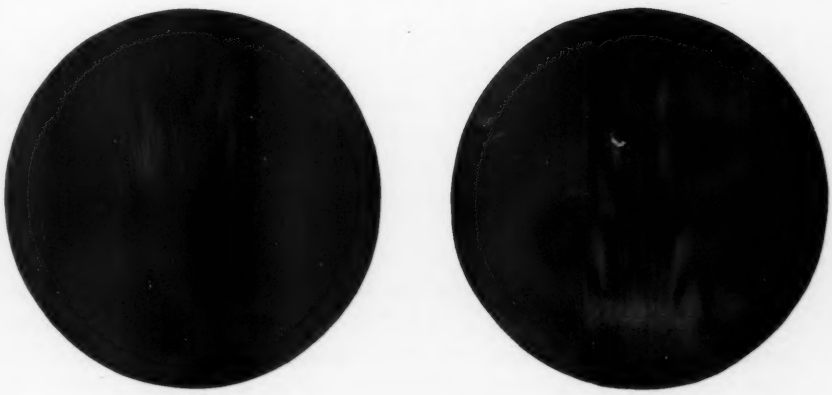


FIG. 4.

Form of sound field at various supersonic intensities; (*a*) 150 mA; (*b*) 250 mA; (*c*) 400 mA; (*d*) 500 mA in the oscillatory circuit.



(*e*) (*f*)

FIG. 5.

Form of the sound field.

(*e*) Adjoining the quartz.

(*f*) At a distance from the quartz.

be put analytically as

$$x - x \cos \theta_n = p\lambda \tag{1}$$

where p is an integer. Since

$$\sin \theta_n = n \lambda/\lambda^*,$$

the condition (1) can be put as

$$x \{1 - \sqrt{(1 - n^2 \lambda^2/\lambda^{*2})}\} = p \lambda.$$

Since λ/λ^* is very small and $x\lambda^3/\lambda^{*4}$ and other higher powers are also very small under the usual experimental conditions, we get

$$xn^2\lambda^2/2\lambda^{*2} = p \lambda$$

$$\text{or } x = 2 p \lambda^{*2}/n^2\lambda \tag{2}$$

where p is an integer. In the above we have considered two individual waves, the 0th and the nth, for the sake of simplicity. But we have to consider all the orders given by the integral values of n. If we, however, consider in (2) the values of x when $p = k n^2$ where k is an integer, they will be independent of n and would be common to all the waves. Thus at all distances given by

$$x = 2 k \lambda^{*2}/\lambda$$

where k is an integer, the wave-front will repeat itself. Thus the period for the repetition of the wave-front is $2\lambda^{*2}/\lambda$.

In case we consider standing ultrasonic waves and we are only interested in the *average* form of the wave-front *with respect to time*, it will repeat itself at all distances given by integral multiples of $\lambda^{*2}/2\lambda$.

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STUDIES IN ADSORPTION ON GELS.*

I. A Comparative Study of Selective Adsorption from Binary Mixtures of Liquids on Gels of Silica, Alumina and Ferric Oxide.

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Selective adsorption on silica gel and activated carbon from binary mixtures of liquids has been studied by several workers. Patrick and Jones,[16] working with silica gel, have suggested that the order of increase of adsorption of the solute from a series of solvents is the same as the order of the decrease of the solubility of the solute in the solvents. Jones and Outridge[9] have noticed selective adsorption of *n*-butyl alcohol from benzene-*n*-butyl alcohol-silica gel system. Bartell and co-workers[1,2,3] have worked with carbon and silica gel and explained selective adsorption in relation to adhesion tension data. B. S. Rao[19] after making a study of selective adsorption from various mixtures on silica gel has pointed out how the nature of the liquids employed determines selective adsorption. Doss and B. S. Rao,[6] in a study of "Apparent" and "True" adsorption functions, have discussed the factors underlying selective adsorption. The present paper deals with the influence of gel surface on selective adsorption from liquids. Gels of alumina and ferric oxide were employed in this investigation and the results compared with those obtained on silica gel by B. S. Rao.[19]

Experimental.

Preparation of alumina gel.—To a 0·3 N solution of chemically pure aluminium sulphate kept at 25° C. was added ammonium hydroxide (0·3 N) in a thin stream, the solution being vigorously stirred. According to Yoe[21] the adsorptive capacity of alumina gel is greater the lower the temperature at which it is precipitated. An excess of ammonium hydroxide corresponding to 10% of what was required for complete reaction was employed. The alumina precipitate was filtered over cloth, and washed with distilled water till the filtrate was free from sulphate. It was then dried at 90° C. for 24

* An extract from the dissertation presented by K. Subba Rao in partial fulfilment of the requirements for the Degree of Master of Science of the Mysore University.

hours and the resulting gel which was hard was graded into various sizes. Granules 1 to 2 mm. in diameter were used in the investigation.

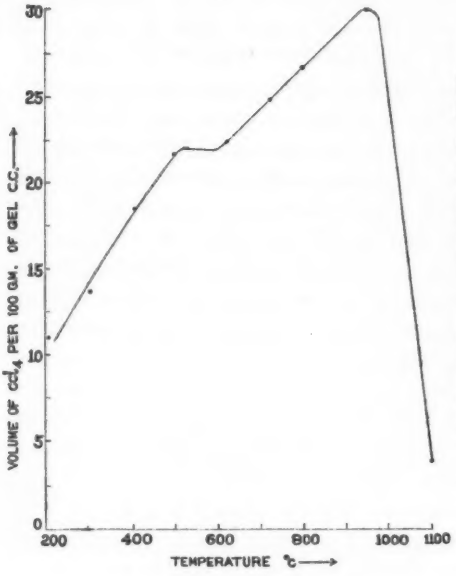
Preparation of ferric oxide gel.—Ferric oxide gel was prepared by mixing 0·5 N ferric chloride solution with 0·5 N ammonium hydroxide solution there being a 25% excess of the latter, the procedure being the same as in the case of alumina gel. The gel was hard and was dark-red in colour.

Activation of alumina gel.—There has been wide variation in the temperature employed by earlier workers in the activation of alumina gel. Chowdhury and Bagchi[5] have activated the gel at 300°–400° C., Perry[18] at 200° C., Munro and Johnson[13,14,15] at 300°–400° C., Wood [20] at 1000° C., Dunstan[7] at 600–700° C. and Bayley[4] at 550° C. An investigation of the optimum temperature of activation of the gel was therefore carried out, employing temperatures ranging from 200° to 1100° C. A current of dry and carbon dioxide-free air was passed over the gel during activation. The adsorptive capacity of the activated gel was determined by passing over the gel kept at 25° C. in a weighed U tube, a current of dry air saturated with carbon tetrachloride vapour, until there was no further increase in the weight of the tube. The volume of carbon tetrachloride adsorbed in each case may be considered to indicate the total volume of the capillaries in the activated gel. Results obtained are shown in Table I.

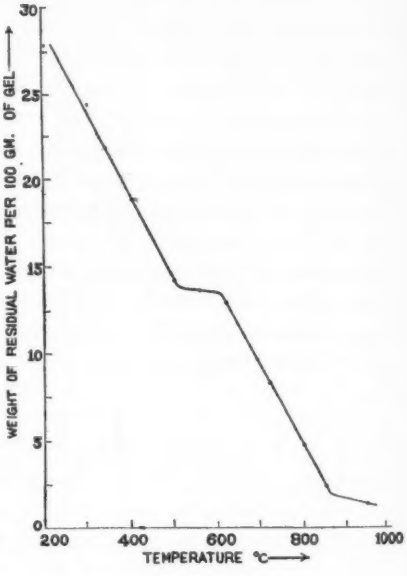
TABLE I.

Temperature of activation of alumina gel in °C.	Volume in c.c. adsorbed per 100 gm. of gel	Weight of residual water in 100 gm. of gel
205	10·97	27·81
305	13·69	24·32
405	18·45	18·83
500	21·58	14·10
620	22·43	12·90
720	24·87	8·25
800	26·62	4·72
850	28·30	2·30
950	29·96	1·47
1100	3·89	..

The relation between the temperature of activation and the volume of carbon tetrachloride adsorbed is represented in Graph 1 and the relation between the temperature and percentage of residual water in Graph 2. Gel activated at 950° C. seems to have the largest capillary space. A safe temperature for effective activation would however be 800° C. Repeated revival of spent gel by activation at 800° C. had no deleterious effect on the capillary space.



GRAPH 1.



GRAPH 2.

The break in the curve in Graph 2 in the neighbourhood of 500° C. is of interest. Between the temperatures 500° C. and 620° C, the gel seems to lose water with difficulty. It is seen also from Table I that at 500° C. increase of temperature of activation to 600° C. does not cause a corresponding increase in capillary space. These observations seem to indicate that part of the water in alumina gel is in the form of a hydrate. It is significant that the phenomenon noticed above occurs when the gel has 14 per cent. water while the monohydrate of alumina has 15 per cent. water.

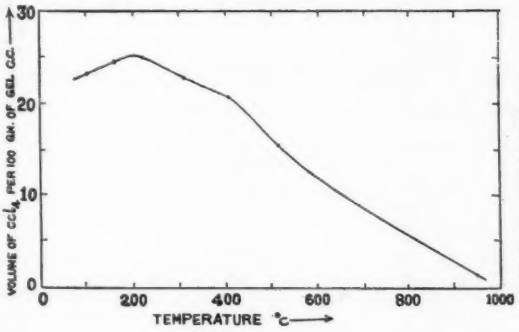
At 900° C. there is a sharp change in the curve in Graph 2. When the temperature of activation is raised beyond 950° C. the capillaries get destroyed and the gel turns chalky white. Structural changes in alumina at

900° C. have been noticed by earlier workers who found the reaction exothermic. The phenomenon has been called calorescence, J. W. Mellor.[12]

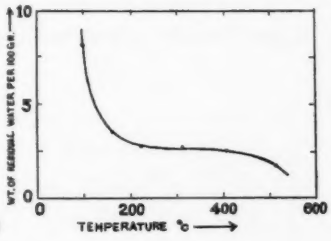
Activation of ferric oxide gel.—Lambert and Clark,[10,11] in studying adsorption hysteresis with ferric oxide, have activated the gel at 170° C. Perry[17] uses in his work ferric oxide gel activated at 230° C. Emmet and Love[8] have found that ferric oxide activated at 550° C. has for water vapour one-fourth the adsorption efficiency of gel activated at 300° C. The optimum temperature of activation for ferric oxide was determined by the method employed for alumina gel. The results are shown in Table II.

TABLE II.

Temperature of activation of ferric oxide gel in °C.	Volume in c.c. of carbon tetrachloride adsorbed per 100 gm. of gel	Weight of residual water in 100 gm. of gel
100	23·10	8·19
160	24·56	3·51
220	25·00	2·72
310	22·86	2·90
405	20·82	2·61
510	15·61	1·74
950	1·15	..



GRAPH 3.



GRAPH 4.

With reference to Graph 3, gel activated at 220° C. has the maximum adsorptive capacity and the adsorptive capacity diminishes as the temperature of activation is increased. A temperature of 180°–200° C. seems to be most suitable for activation of ferric oxide. Relation between the temperature of activation and the percentage of residual water in the gel is shown in Graph 4. As with alumina, repeated revival of spent gel did not affect the adsorptive capacity.

Adsorption experiments.—The organic liquids employed in the work were purified by standard methods. The following mixtures were used:

1. Ethyl alcohol and benzene.
2. Ethyl alcohol and carbon tetrachloride.
3. Ethyl alcohol and water.
4. Water and pyridine.
5. Benzene and carbon tetrachloride.

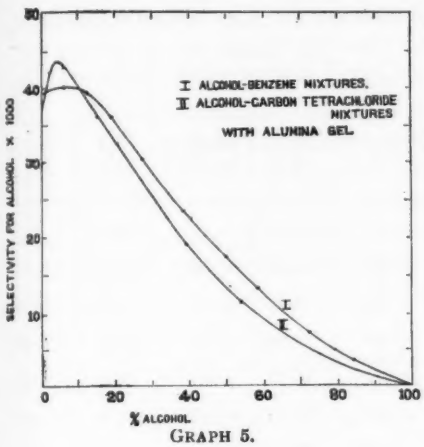
Procedure.—A known weight (7 to 8 gm.) of the activated gel was dropped into a small " sample tube " containing a known weight (4 to 5 gm.) of the binary mixture. To avoid heat effects during adsorption the tube was cooled in ice. Samples of the liquid were withdrawn for analysis after the tube had been kept in a thermostat at 25° C. for 12 hours. The composition of the liquid was determined with the aid of a Pulfrich refractometer.

Selective adsorption on the gel is expressed by the term " Selectivity " given by the relation,

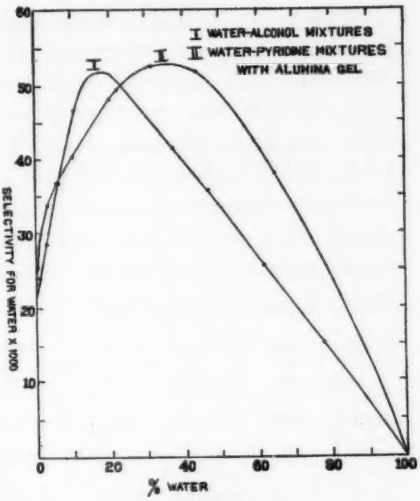
$$S = \frac{w\,(c_i - c_l)}{100\,m}$$ (B. S. Rao[19])

where S = Selectivity.
w = weight of the liquid mixed with the gel.
c_i = the initial composition of the liquid mixture in weight per cent.
c_l = the final composition of the liquid mixture in weight per cent.
m = weight of the gel.

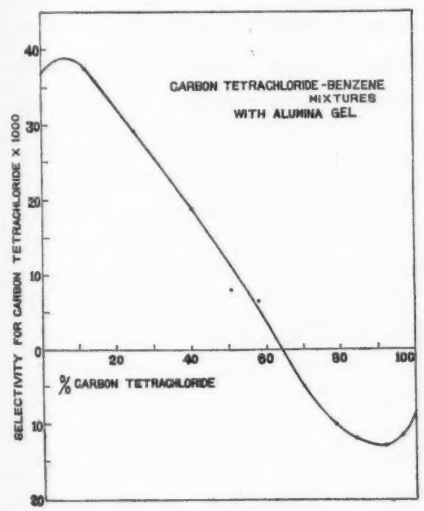
The results obtained are given in Tables III and IV and the selectivity-concentration curves in Graphs 5 to 10.



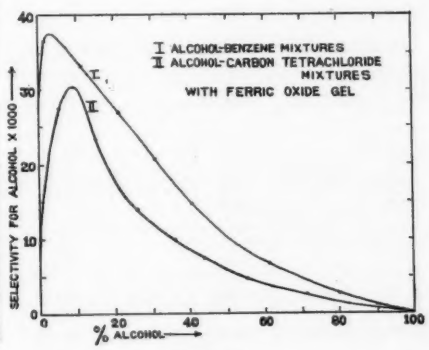
GRAPH 5.



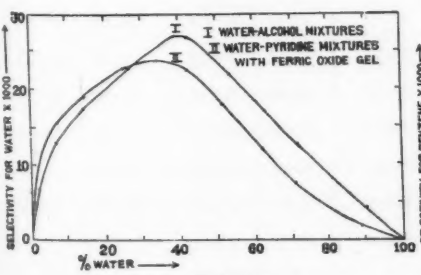
GRAPH 6.



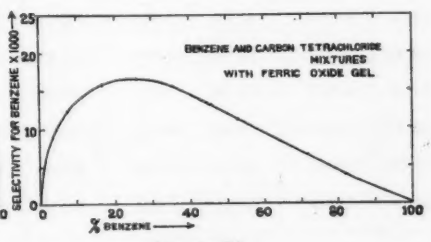
GRAPH 7.



GRAPH 8.



GRAPH 9.



GRAPH 10.

TABLE III. *Selective adsorption on alumina gel from binary mixtures.*

EtOH and C_6H_6		EtOH and CCl_4		EtOH and H_2O		H_2O and Pyridine		C_6H_6 and CCl_4	
p.c. of Et OH	Selectivity for EtOH	p.c. of EtOH	Selectivity for EtOH	p.c. of H_2O	Selectivity for H_2O	p.c. of H_2O	Selectivity for H_2O	p.c. of CCl_4	Selectivity for CCl_4
C_l		C_l		C_l		C_l		C_l	
1·10	0·039	2·40	0·042	1·15	0·024	0·95	0·026	12·25	+0·037
6·15	0·040	6·60	0·043	3·60	0·029	3·45	0·034	25·30	+0·029
12·35	0·039	9·15	0·040	6·70	0·037	6·30	0·037	40·70	+0·019
19·15	0·036	15·70	0·036	10·85	0·047	10·25	0·040	50·80	+0·008
27·70	0·030	20·75	0·032	27·30	0·029	19·80	0·048	57·95	+0·006
38·50	0·024	30.70	0·024	37·00	0·041	21·65	0·050	69·80	−0·005
49·55	0·017	39·65	0·019	46·90	0·036	31·35	0·053	78·65	−0·010
58·40	0·013	53·95	0·012	61·65	0·026	43·20	0·052	84·00	−0·012
72·15	0·008	77·00	0·001	78·00	0·015	64·50	0·038	91·65	−0·013
83·80	0·004							96·50	−0·011

TABLE IV. *Selective adsorption on ferric oxide gel from binary mixtures.*

EtOH and C_6H_6		EtOH and CCl_4		EtOH and H_2O		H_2O and Pyridine		C_6H_6 and CCl_4	
p.c. of Et OH	Selectivity for EtOH	p.c. of EtOH	Selectivity for EtOH	p.c. of H_2O	Selectivity for H_2O	p.c. of H_2O	Selectivity for H_2O	p.c. of C_6H_6	Selectivity for C_6H_6
C_l		C_l		C_l		C_l		C_l	
1·50	0·037	5·65	0·028	7·10	0·013	7·65	0·016	7·95	0·012
11·25	0·033	14·95	0·023	14·25	0·018	14·66	0·019	16·85	0·016
21·25	0·027	25·70	0·014	26·66	0·013	24·90	0·023	26·00	0·017
30·70	0·021	35·33	0·010	32·70	0·027	33·60	0·024	35·50	0·016
40·35	0·015	43·35	0·008	42·70	0·027	42·35	0·022	45·50	0·013
49·00	0·014	54·90	0·005	53·85	0·022	51·40	0·018	52·90	0·011
60·85	0·007	61·90	0·004	63·30	0·013	62·45	0·012	60·50	0·007
69·25	0·006	71·00	0·003	71·40	0·013	70·90	0·007	71·90	0·007
80·00	0·003	82·00	0·003	81·00	0·008	81·60	0·004	81·70	0·004
89·35	0·001	90·60	0·001	90·30	0·004	88·75	0·002		

Discussion.

Alcohol is selectively adsorbed on alumina and ferric oxide gels from alcohol-benzene and alcohol-carbon tetrachloride mixtures, over the entire range of concentrations. This is analogous to the behaviour of silica gel as studied by B. S. Rao[19] and Doss and B. S. Rao.[6] Alumina and ferric oxide, however, differ from silica gel in their behaviour towards alcohol-water mixtures. Silica gel gives the S-type selectivity-concentration curve, there being selective adsorption of alcohol in dilute alcoholic solutions and selective adsorption of water from concentrated solutions, while alumina and ferric oxide gels give the U-type curves indicating selective adsorption of water at all concentrations.

Silica gel gives with pyridine-water mixtures the S-type curve (B. S. Rao[19] and Doss and B. S. Rao[6]), with alumina and ferric oxide gels U-type curves are obtained, water being selectively adsorbed at all concentrations. This denotes that pyridine is more strongly adsorbed by silica than by alumina or ferric oxide gels, a fact which can be correlated with the acidic nature of silica surface.

There is a notable difference also in the behaviour of the three gels towards benzene-carbon tetrachloride mixtures. With silica and ferric oxide gels, there is selective adsorption of benzene throughout and U-type curves are obtained. Alumina gel however gives the S-type curve and in fact the curve indicates for alumina a higher selectivity for carbon tetrachloride. This is presumably due to an attraction between the aluminium of the gel and the chlorine atoms of the adsorbed liquid.

Doss and Rao[6] have suggested that the S-shaped curve is probably caused by the preferential adsorption of molecular compounds of the components of the binary mixture. In agreement with this point of view they found that the mixture giving zero selectivity in pyridine-water-silica system has a composition closely corresponding to the mono-hydrate. We have obtained similar results with carbon tetrachloride-benzene mixtures. The composition of the mixture giving zero selectivity corresponds approximately to C_6H_6, CCl_4. It is interesting to note that alumina gel turns black when immersed in benzene-carbon tetrachloride mixtures, while the gel suffers no such colour change when immersed in either benzene or carbon tetrachloride. On addition of water the gel loses the black colour owing to the desorption of the benzene-carbon tetrachloride mixture. The blackening effect is being investigated in this laboratory.

In conclusion, it may be stated that the adsorption of liquids on gels of silica, alumina and ferric oxide, is not to be looked upon as mere capillary

condensation, but that the chemical nature of the gel has a marked influence on selective adsorption from binary mixtures of liquids.

Summary.

The effect of temperature of activation on the capillary space in alumina and ferric oxide gels has been studied. Structural changes in alumina gel have been noticed in the neighbourhood of 500° C. and 900° C. and their significance discussed.

Adsorption on alumina and ferric oxide gels from binary mixtures of liquids has been studied and the behaviour of these has been compared with that of silica. It is concluded that the chemical nature of a gel markedly affects selective adsorption from binary mixtures of liquids.

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21. Yoe .. .. *J. Phys. Chem.*, 1925, **29**, 1419.

Page 571, para 1, line 2—

for $\prod_{i=1}^{k}$ *read* $\prod_{i=0}^{k}$

ON SUMS OF POWERS.*

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(*From the Government College, Hoshiarpur.*)

Received September 21, 1936.

(Communicated by Dr. B. L. Bhatia.)

1. Consider the function

$$f_k(x) \equiv \psi_k(x) \cdot \prod_{i=1}^{k} (x^{d_i} - 1), \quad \psi_k(1) \neq 0 \qquad \ldots \qquad \ldots \qquad (1)$$

where $\psi_k(x)$ is a polynomial in x with integral coefficients, and the d's are positive integers $\geqslant 1$.

If we expand the right hand side of (1), we get on simplification

$$f_k(x) \equiv \sum_{i=1}^{n} (x^{a_i} - x^{b_i}),$$

where the a's and b's are integers $\geqslant 0$, which satisfy the equations :

$$a_1^m + a_2^m + a_3^m + \cdots + a_n^m = b_1^m + b_2^m + b_3^m + \cdots + b_n^m \ldots \qquad (2)$$

where $m = 1, 2, 3, \ldots k$, but $\neq k+1$.

After Wright,[1] we shall call (1) the generating polynomial of (2). For brevity, we shall write (2) in the form :

$$A \underset{=}{\overset{k}{=}} B, \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad (3)$$

A denoting the set of integers $a_1, a_2, a_3, \ldots a_n$; and B denoting the set of integers $b_1, b_2, b_3, \ldots b_n$.

In what follows, M (k) denotes the least value of n, for which solutions of (3) exist for a given value of k. Capital letters are used to denote sets of integers, while small letters stand for integers.

If C be a set of i integers and D a set of j integers, then we denote by $C \oplus D$ the set of ij integers obtained by adding each of the elements of set C to each of the elements of set D. We write in a similar manner, $C \ominus D$ to denote a set of ij integers obtained by subtracting each element of D from each element of C.

Tarry has observed that (3) implies :

$$A, B \oplus h \underset{=}{\overset{k+1}{=}} B, A \oplus h, \qquad h \geqslant 1 \qquad \ldots \qquad \ldots \qquad \ldots \qquad (4)$$

the generating polynomial for (4) being $(x^h - 1) f_k(x)$.

---

* I have received considerable help in the preparation of this paper from my younger brother Dinanath Gupta.

[1] E. M. Wright, "On Tarry's Problem," *Quar. Jour. of Maths.*, 1936, 7, 43–45.

Notice that (3) also implies

$$A \oplus C \underset{=}{k} B \oplus C \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

If $C \equiv c_1, c_2, c_3, \ldots . c_t$;

then the generating polynomial for (5) is $f_k(x) . \sum_{i=1}^{t} x^{c_i}$.

Wright,[2] Chowla,[3] Sastry,[4] and Moessner and Schulz,[5] have made use of (4) in finding upper bounds for the values of $M(k)$. My chief object in this note is to improve upon the results given by these authors. In this connection, it is noteworthy that (5) can be used with advantage.

2. Applying (4) to :

$$1 \underset{=}{0} 2$$

with $h = 2, 3, 5, 7, 8, 11, 13, 9, 19, 17, 6, 4, 15$, in succession,[6] we get[7]

$$A_1, 122 \ominus A_1 \underset{=}{13} B_1, 122 \ominus B_1, \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where $A_1 \equiv 1, 6, 8, 11, 18, 20, 21, 22, 29, 31, 32, 42, 43, 47, 52, 54$;

and $B_1 \equiv 2, 3, 12, 13, 14, 16, 23, 25, 26, 35, 36, 37, 39, 46, 56, 60$.

Applying (5) to (6), with $C \equiv 0, 6, 8, 14$; or with $C \equiv 0, 8$; and $0, 6$; in succession, we obtain :

$$A_2, 136 \ominus A_2 \underset{=}{13} B_2, 136 \ominus B_2, \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where $A_2 \equiv 1, 6, 7, 14, 15, 28, 29, 32, 35, 38, 48, 55, 57, 58, 61$;

and $B_2 \equiv 2, 3, 10, 13, 16, 23, 31, 33, 39, 41, 44, 45, 62, 64, 66$.

Hence $M(13) \leqslant 30$. Previous results were :

$M(13) \leqslant 34$, (Chowla) ; $M(13) \leqslant 32$, (Sastry, Moessner and Schulz).

3. Applying (4) to (6) with $h = 10$, we get[7]

$$A_3 \underset{=}{14} 132 \ominus A_3, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

where $A_3 \equiv 1, 6, 8, 20, 22, 22, 24, 29, 33, 43, 45, 47, 47, 49, 54, 68, 70, 70, 72, 75, 79, 91, 93, 93, 95, 102, 104, 107, 116, 116, 118, 129, 130.$

Applying (5) to (8) with $C \equiv 0, 8$; we get

$$A_4 \underset{=}{14} 140 \ominus A_4, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

where $A_4 \equiv 1, 6, 8, 9, 20, 22, 29, 30, 32, 43, 51, 54, 55, 55, 75, 76, 78, 79, 80, 101, 101, 102, 104, 115, 116, 124, 129, 130, 137, 138.$

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2 *Jour. London Math. Soc.*, 1934, **9**, 267–272.

3 *Proc. Ind. Acad. Sci.*, 1935, **1**, 528–530.

4 *Proc. Ind. Acad. Sci.*, 1935, **1**, 928–929.

5 *Math. Ztschr.*, 1936, **41**, 340–344.

6 The order does not affect the final result.

7 These results occur in 5.

Thus M (14) $\leqslant$ 30. Previous results were :

M (14) $\leqslant$ 33, (Moessner and Schulz).

M (14) $\leqslant$ 46, (Chowla) ; M (14) $\leqslant$ 34, (Sastry) ;

4. Apply (4) to (8), with $h = 23, 25, 27, 21, 31, 29$, in succession, (the order is relevant) ; then we obtain

(*i*) A_5, $155 \ominus A_5 \overset{15}{\equiv} B_5$, $155 \ominus B_5$, ... (10)

where $A_5 \equiv$ 1, 6, 8, 20, 22, 22, 26, 33, 47, 48, 49, 51, 54, 75, 76 ;

and $B_5 \equiv$ 2, 3, 14, 16, 16, 28, 30, 31, 41, 45, 52, 56, 57, 66, 77.

Hence M (15) $\leqslant$ 30. Previous results were :

M (15) $\leqslant$ 44, (Chowla) ; M (15) $\leqslant$ 34, (Sastry).

(*ii*) $A_6 \overset{16}{\equiv} 180 \ominus A_6$, ... (11)

where $A_6 \equiv$ 1, 6, 8, 20, 22, 22, 27, 39, 41, 48, 49, 53, 54, 55, 70, 75, 80, 81, 82, 91, 102, 106, 107, 108, 122, 123, 128, 133, 135, 135, 149, 149, 150, 164, 164, 166, 177, 178 ;

so that M (16) $\leqslant$ 38. Previous results were :

M (16) $\leqslant$ 54, (Chowla) ; M (16) $\leqslant$ 46, (Sastry.)

(*iii*) A_7, $207 \ominus A_7 \overset{17}{\equiv} B_7$, $207 \ominus B_7$, ... (12)

where $A_7 \equiv$ 1, 6, 8, 20, 22, 22, 27, 29, 39, 41, 41, 43, 43, 48, 53, 55, 58, 70, 72, 79, 84, 85, 91, 101 ;

and $B_7 \equiv$ 2, 3, 14, 16, 16, 28, 31, 31, 33, 35, 45, 45, 47, 47, 49, 52, 66, 68, 73, 76, 78, 89, 97, 98.

Thus M (17) $\leqslant$ 48. Previous results were :

M (17) $\leqslant$ 70, (Chowla) ; M (17) $\leqslant$ 56, (Sastry).

(*iv*) $A_8 \overset{18}{\equiv} 228 \ominus A_8$, ... (13)

where $A_8 \equiv$ 1, 6, 8, 20, 22, 23, 24, 37, 37, 39, 41, 52, 53, 54, 55, 56, 58, 66, 68, 70, 70, 72, 84, 85, 87, 94, 99, 101, 116, 119, 123, 128, 130, 135, 150, 152, 152, 154, 159, 164, 164, 166, 166, 168, 178, 181, 181, 183, 183, 195, 197, 197, 200, 212, 212, 214, 225, 226.

This gives M (18) $\leqslant$ 58. Previous results were :

M (18) $\leqslant$ 80, (Wright) ; M (18) $\leqslant$ 68, (Chowla) ; M (18) $\leqslant$ 60, (Sastry).

(*v*) A_9, $259 \ominus A_9 \overset{19}{\equiv} B_9$, $259 \ominus B_9$, ... (14)

where $A_9 \equiv$ 1, 6, 8, 20, 22, 23, 24, 34, 37, 41, 52, 56, 58, 59, 66, 70, 78, 81, 91, 93, 94, 95, 95, 107, 107, 119, 123, 124, 128 ;

and $B_9 \equiv$ 2, 3, 14, 16, 16, 28, 31, 31, 32, 45, 50, 51, 60, 64, 68, 69, 74, 83, 86, 89, 97, 98, 101, 103, 112, 115, 118, 125, 127.

Hence M (19) $\leqslant$ 58.

(*vi*) $A_{10} \overset{20}{\equiv} 288 \ominus A_{10}$, ... (15)

where $A_{10} \equiv$ 1, 6, 8, 20, 22, 23, 24, 34, 41, 43, 45, 56, 57, 58, 59, 60, 61, 78, 79, 80, 91, 93, 93, 94, 95, 107, 119, 126, 128, 130, 131, 135, 140, 152, 154, 163, 164, 166, 168, 178, 187, 189, 200, 201,

202, 203, 205, 219, 220, 224, 225, 235, 237, 237, 238, 239, 253, 257, 258, 260, 272, 272, 274, 285, 286.

Now applying (5) to (15), with C ≡ 0, 8, we get

$$A_{11} \overset{20}{\equiv} 296 \ominus A_{11}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (16)$$

where $A_{11} \equiv$ 1, 6, 8, 9, 20, 23, 32, 34, 41, 42, 45, 56, 60, 65, 66, 67, 78, 79, 80, 93, 101, 102, 103, 115, 119, 126, 127, 131, 135, 138, 139, 140, 143, 152, 154, 163, 164, 171, 172, 174, 176, 178, 186, 187, 200, 211, 213, 219, 220, 224, 225, 233, 237, 245, 246, 257, 258, 260, 261, 272, 280, 285, 286, 293, 294.

From (15) or (16), it follows that $M(20) \leqslant 65$.

(16) is noteworthy in so far as none of the elements on either side is repeated.

5. If we write $\beta(k)$ for the least value of s for which the equation :

$$a_1^k + a_2^k + a_3^k + \ldots + a_t^k = b_1^k + b_2^k + b_3^k + \ldots + b_s^k,$$

has a solution, with $t < s$, and $(a_1, a_2, a_3, \ldots a_t) = (b_1, b_2, b_3, \ldots b_s) = 1$, then from the results given in the preceding sections, it is easy to prove that

$$\beta(13) \leqslant 16\,; \quad \beta(17) \leqslant 30\,; \quad \beta(19) \leqslant 33.$$

Moessner and Schulz gave $\beta(13) \leqslant 18$.

Again applying (5) to (11) with C = − 86, we obtain

$$3^k + 4^k + 6^k + 11^k + 19^k + 24^k + 31^k + 32^k + 33^k + 38^k + 40^k + 45^k + 45^k + 46^k + 53^k + 59^k + 64^k + 66^k + 67^k + 72^k + 74^k + 85^k + 86^k + 88^k + 93^k.$$

$$= 8^k + 20^k + 21^k + 22^k + 28^k + 29^k + 34^k + 36^k + 41^k + 42^k + 49^k + 49^k + 55^k + 56^k + 63^k + 63^k + 70^k + 70^k + 78^k + 83^k + 84^k + 91^k + 92^k,$$

where $k = 1, 3, 5, 7, 9, 11, 13, 15.$

Hence $\beta(15) \leqslant 25.$

COMPLEX REPRESENTATION IN BORN'S FIELD THEORY.

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1. *Introduction.*

Schrödinger[1] has given a representation of Born's field theory by using two complex combinations of **B**, **E**, **H**, **D**

$$\mathcal{F} = \mathbf{B} - i\mathbf{D}\,;\ \mathcal{G} = \mathbf{E} + i\mathbf{H}, \quad \ldots \quad (1)$$

starting with the Lagrangian

$$\mathcal{L} = \frac{\mathcal{F}^2 - \mathcal{G}^2}{(\mathcal{F}\mathcal{G})} \quad \ldots \quad (2)$$

and the "condition of conjugateness" given by

$$\left.\begin{aligned} \mathcal{F}^* &= \frac{\partial \mathcal{L}}{\partial \mathcal{G}} = -\frac{2\mathcal{G}}{(\mathcal{F}\mathcal{G})} - \frac{\mathcal{F}^2 - \mathcal{G}^2}{(\mathcal{F}\mathcal{G})^2}\,\mathcal{F} \\ \mathcal{G}^* &= \frac{\partial \mathcal{L}}{\partial \mathcal{F}} = \frac{2\mathcal{F}}{(\mathcal{F}\mathcal{G})} - \frac{\mathcal{F}^2 - \mathcal{G}^2}{(\mathcal{F}\mathcal{G})^2}\,\mathcal{G} \end{aligned}\right\} \quad \ldots \quad (3)$$

The equivalence of this treatment with Born's theory is shown by using suitable Lorentz and γ-transformations and reducing both representations to a common form. In this paper, I have established this equivalence directly by means of analytical transformations by showing that (3) is an exact transcription of Born's relations between primary and secondary field vectors and also given two other simple proofs of this equivalence. This has necessitated a detailed study of the invariants of Born's and Schrödinger's representations and as a result I have been able to find two other alternative complex representations (entirely equivalent to Schrödinger's) in which the action function again appears with the square root. The results obtained in this paper are summarised as follows :—

(1) If $\mathcal{G}^* = \frac{\partial \mathcal{L}}{\partial \mathcal{F}}$ and $\mathcal{F}^* = \frac{\partial \mathcal{L}}{\partial \mathcal{G}}$ and Born's relations hold between the real field vectors, then $\mathcal{L}$ has necessarily the form (2).

(2) A detailed study is made of the relations between the several invariants and space invariants of Born's theory.

[1] E. Schrödinger, *Proc. Roy. Soc.*, A, 1935, **150**, 465.

(3) A similar study is made of the invariants of Schrödinger's representation and its equivalence with Born's representation is exhibited analytically.

(4) It is shown that Schrödinger's representation is equivalent to the alternative representations

$$\left.\begin{aligned}\frac{\partial \mathcal{U}}{\partial \mathcal{F}} &= \mathcal{G}^* \\ \frac{\partial \mathcal{U}}{\partial \mathcal{F}^*} &= -\mathcal{G}\end{aligned}\right\} \text{ and } \left.\begin{aligned}\frac{\partial \mathcal{V}}{\partial \mathcal{G}} &= \mathcal{F}^* \\ \frac{\partial \mathcal{V}}{\partial \mathcal{G}^*} &= -\mathcal{F}\end{aligned}\right\}$$

where $\mathcal{U}$ and $\mathcal{V}$ are functions respectively of $\mathcal{F}$, $\mathcal{F}^*$ and $\mathcal{G}$, $\mathcal{G}^*$ with a square root form. These representations lead in the simplest manner to the form (2) of Schrödinger's Lagrangian.

2. *Form of Schrödinger's Lagrangian.*

We will show that if $\mathcal{G}^* = \frac{\partial \mathcal{L}}{\partial \mathcal{F}}$ and $\mathcal{F}^* = \frac{\partial \mathcal{L}}{\partial \mathcal{G}}$ and if Born's relations hold between the field components, then $\mathcal{L}$ has necessarily the form (2).

If $\mathcal{F}$ and $\mathcal{G}$ are defined by (1), they form a true six vector defined by the antisymmetric tensor

$$q_{kl} = f_{kl} - ip_{kl}^* \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

where the tensors f_{kl} and p_{kl} define the field components of Born's theory.[2] The complex conjugates[3] $(\mathcal{G}^*, \mathcal{F}^*)$ also form a true six vector defined by the antisymmetric tensor

$$r^{kl} = f^{*kl} - ip^{kl} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

and the equations

$$\mathcal{G}^* = \frac{\partial \mathcal{L}}{\partial \mathcal{F}}\ ;\ \mathcal{F}^* = \frac{\partial \mathcal{L}}{\partial \mathcal{G}}$$

can be written in the form

$$r^{kl} = \frac{\partial \mathcal{L}}{\partial q_{kl}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

With $\mathcal{L}$ we can associate, just as in Born's theory, a Hamiltonian $\mathcal{H}$ given by

$$\mathcal{H} = \mathcal{L} - \tfrac{1}{2} r^{kl} q_{kl} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

Following the notation of Born and Infeld we shall use the relations[4]

$$\frac{1 + \mathrm{F} - \mathrm{G}^2}{1 + \mathrm{G}^2} = \frac{1 + \mathrm{Q}^2}{1 + \mathrm{P} - \mathrm{Q}^2} \quad .. \quad .. \quad .. \quad .. \quad (8)$$

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[2] *i.e.*, $(p_{23}, p_{31}, p_{12}) \rightarrow \mathbf{H}$; $(f_{23}, f_{31}, f_{12}) \rightarrow \mathbf{B}$
$(p_{14}, p_{24}, p_{34}) \rightarrow \mathbf{D}$; $(f_{14}, f_{24}, f_{34}) \rightarrow \mathbf{E}$

[3] The * indicates the dual when associated with a tensor and the complex conjugate when referring to a vector.

[4] Born and Infeld, *Proc. Roy. Soc.*, A, 1934, **144**, 435.

$$G = Q \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

which hold between the several invariants. Calculating the second term on the right-hand side of (7), by using (1),

$$\tfrac{1}{2}\, r^{kl} q_{kl} = (\mathbf{E} - i\,\mathbf{H})\,(\mathbf{B} - i\,\mathbf{D}) + (\mathbf{B} + i\,\mathbf{D})\,(\mathbf{E} + i\,\mathbf{H})$$
$$= 2\,(G - Q) = 0, \text{ using (9)} \quad .. \quad .. \quad .. \quad (10)$$

Hence $\mathcal{H} = \mathcal{L}$ or, *in Schrödinger's representation the Hamiltonian coincides with the Lagrangian*; and corresponding to (6) we also have

$$q^{*kl} = \frac{\partial \mathcal{L}}{\partial r^*_{kl}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11)$$

where $\mathcal{L}$ is defined as a function of the invariants associated with r^{kl}. In (6) let $\mathcal{L}$ be considered a function of the two invariants f and g, where

$$\left.\begin{aligned} f &= \mathcal{F}^2 - \mathcal{G}^2 = \tfrac{1}{2}\, q_{kl}\, r^{kl} \\ g &= (\mathcal{F}\,\mathcal{G}) = \tfrac{1}{4}\, q_{kl}\, q^{*kl} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (12)$$

and in (11) as a function of the two invariants p and q, where

$$\left.\begin{aligned} p &= \mathcal{G}^{*2} - \mathcal{F}^{*2} = \tfrac{1}{2}\, r_{kl}\, r^{kl} \\ q &= (\mathcal{G}^*\,\mathcal{F}^*) = -\tfrac{1}{4}\, r_{kl}\, r^{*kl} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (13)$$

(6) and (11) can be written in the form

$$r^{kl} = 2\frac{\partial \mathcal{L}}{\partial f}\, q^{kl} + \frac{\partial \mathcal{L}}{\partial g}\, q^{kl} \quad .. \quad .. \quad .. \quad .. \quad (6, \text{A})$$

$$-\, q^{*kl} = 2\,\frac{\partial \mathcal{L}}{\partial p}\, r^{*kl} + \frac{\partial \mathcal{L}}{\partial q}\, r^{kl} \quad .. \quad .. \quad .. \quad .. \quad (11, \text{A})$$

By direct calculation, using (4) and (5) we can easily deduce

$$\tfrac{1}{2}\, r^{kl} q_{kl}^* = \tfrac{1}{2}\, r^{*kl} q_{kl} = \tfrac{1}{2}\, r_{kl} q^{*kl} = \tfrac{1}{2}\, r_{kl}^* q^{kl} = -\,(\mathbf{F} + \mathbf{P}) \quad .. \quad (14)$$

We now multiply (6, A) respectively by $\frac{1}{4}\, q_{kl}$, $\frac{1}{4}\, r_{kl}^*$ and $\frac{1}{2}\, r_{kl}$ and sum up in each case. In view of (14), this gives the relations

$$\left.\begin{aligned} f\frac{\partial \mathcal{L}}{\partial f} + g\frac{\partial \mathcal{L}}{\partial g} &= 0 \\ \frac{\partial \mathcal{L}}{\partial f} &= \frac{q}{\mathbf{F} + \mathbf{P}} \\ \frac{\partial \mathcal{L}}{\partial g} &= -\,\frac{p}{\mathbf{F} + \mathbf{P}} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (15)$$

Treating (11, A) in exactly the same way by multiplying by $\frac{1}{4}\, r_{kl}^*$, $\frac{1}{4}\, q_{kl}$ and $\frac{1}{2}\, q_{kl}^*$ and summing up, we get

$$\left.\begin{aligned} p\,\frac{\partial \mathcal{L}}{\partial p} + q\frac{\partial \mathcal{L}}{\partial q} &= 0 \\ \frac{\partial \mathcal{L}}{\partial p} &= \frac{g}{\mathbf{F} + \mathbf{P}} \\ \frac{\partial \mathcal{L}}{\partial q} &= -\,\frac{f}{\mathbf{F} + \mathbf{P}} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (16)$$

From the first of the equations in (15) or (16) we see that $\mathcal{L}$ is a homogeneous function of degree zero in (f, g) or (p, q), which is also otherwise obvious from the relation (10) or its equivalent

$$(\mathcal{F}\,\mathcal{G}^*) + (\mathcal{F}^*\mathcal{G}) = 0.$$

Also from either (15) or (16) we get

$$\frac{f}{g} = \frac{p}{q} \qquad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (17)$$

We now proceed to calculate actually the values of the partial derivatives of $\mathcal{L}$ by making use of Born's relation (8). If L and H be the Lagrangian and Hamiltonian of Born's theory

$$\left.\begin{aligned} \mathrm{L} &= \sqrt{1 + \mathrm{F} - \mathrm{G}^2} - 1 \\ \mathrm{H} &= \sqrt{1 + \mathrm{P} - \mathrm{Q}^2} - 1 \\ \mathrm{H} &= \mathrm{L} - \mathrm{R} \end{aligned}\right\}$$

and using these expressions (8) can be written alternatively as

$$(\mathrm{L} + 1)(\mathrm{H} + 1) = 1 + \mathrm{G}^2 \qquad .. \quad .. \quad .. \quad .. \quad (18)$$

From (1) we get

$$g = \mathrm{G} + \mathrm{Q} + i\mathrm{R} = 2\mathrm{G} + i\mathrm{R}$$
$$q = \mathrm{G} + \mathrm{Q} - i\mathrm{R} = 2\mathrm{G} - i\mathrm{R},$$

hence,

$$\begin{aligned} gq &= 4\mathrm{G}^2 + \mathrm{R}^2 = 4\mathrm{G}^2 + [(\mathrm{L} + 1) - (\mathrm{H} + 1)]^2 \\ &= 4\mathrm{G}^2 + (\mathrm{L} + 1)^2 + (\mathrm{H} + 1)^2 - 2(1 + \mathrm{G}^2), \text{ from (18)} \\ &= 4\mathrm{G}^2 + (1 + \mathrm{F} - \mathrm{G}^2) + (1 + \mathrm{P} - \mathrm{Q}^2) - 2(1 + \mathrm{G}^2) \end{aligned}$$

$$\therefore \quad gq = \mathrm{F} + \mathrm{P} \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (19)$$

Substituting (19) in the second equations of (15) and (16),

$$\frac{\partial \mathcal{L}}{\partial f} = \frac{1}{g}; \quad \frac{\partial \mathcal{L}}{\partial p} = \frac{1}{q}$$

and the first equations of the same two sets show that

$$\frac{\partial \mathcal{L}}{\partial g} = -\frac{f}{g^2}; \quad \frac{\partial \mathcal{L}}{\partial q} = -\frac{p}{q^2}$$

Hence,

$$\mathcal{L} = \frac{f}{g} = \frac{p}{q} \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (20)$$

which is the same as (2). Equation (20) consists of both the equations (1) and (6) of Schrödinger's paper.

3. *Relations between Born's Invariants.*

The invariants F, G, P, Q, R, S are defined by the relations

$$\mathrm{F} = \tfrac{1}{2} f^{kl} f_{kl} = -\tfrac{1}{2} f^{*kl} f^*_{kl}; \quad \mathrm{P} = \tfrac{1}{2} p_{kl}{}^* p^{*kl} = -\tfrac{1}{2} p_{kl}\, p^{kl};$$
$$\mathrm{G} = \tfrac{1}{4} f_{kl} f^{*kl} = \tfrac{1}{4} f_{kl}{}^* f^{kl}; \qquad \mathrm{Q} = \tfrac{1}{4} p^{kl} p_{kl}{}^* = \tfrac{1}{4} p^{*kl} p_{kl};$$
$$\mathrm{R} = \tfrac{1}{2} f_{kl}\, p^{kl} = -\tfrac{1}{2} f^*_{kl}\, p^{*kl}; \quad \mathrm{S} = \tfrac{1}{2} f^{kl}\, p_{kl}{}^* = \tfrac{1}{2} f^{*kl}\, p_{kl};$$

or, in space vector notation,

$$F = \mathbf{B}^2 - \mathbf{E}^2\,;\ P = \mathbf{D}^2 - \mathbf{H}^2\,;\ G = (\mathbf{B}\,\mathbf{E})\,;\ Q = (\mathbf{D}\,\mathbf{H})\,;$$
$$R = (\mathbf{B}\,\mathbf{H}) - (\mathbf{D}\,\mathbf{E})\,;\ S = (\mathbf{B}\,\mathbf{D}) + (\mathbf{E}\,\mathbf{H}).$$

We shall derive the several relations that exist between these invariants.
In the equations

$$\left.\begin{aligned} p^{kl} &= 2\frac{\partial L}{\partial F} f^{kl} + \frac{\partial L}{\partial G} f^{*kl} \\ f^{*kl} &= 2\frac{\partial H}{\partial P} p^{*kl} + \frac{\partial H}{\partial Q} p^{kl} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (21)$$

multiply the first respectively by $\frac{1}{2}f_{kl}$, $\frac{1}{2}f_{kl}^*$, $\frac{1}{2}p_{kl}$, $\frac{1}{4}\ p_{kl}^*$ and sum up; similarly the second by $\frac{1}{4}f_{kl}$, $\frac{1}{2}f_{kl}^*$, $\frac{1}{2}p_{kl}$, $\frac{1}{2}p_{kl}^*$ and sum up. We then get

$$\left.\begin{aligned} R &= 2F\frac{\partial L}{\partial F} + 2G\frac{\partial L}{\partial G} \\ S &= 4G\frac{\partial L}{\partial F} - F\frac{\partial L}{\partial G} \\ -P &= 2R\frac{\partial L}{\partial F} + S\frac{\partial L}{\partial G} \\ Q &= S\frac{\partial L}{\partial F} - \frac{R}{2}\frac{\partial L}{\partial G} \end{aligned}\right| \qquad \left|\begin{aligned} G &= S\frac{\partial H}{\partial P} + \frac{R}{2}\frac{\partial H}{\partial Q} \\ -F &= -2R\frac{\partial H}{\partial P} + S\frac{\partial H}{\partial Q} \\ S &= 4Q\frac{\partial H}{\partial P} - P\frac{\partial H}{\partial Q} \\ -R &= 2P\frac{\partial H}{\partial P} + 2Q\frac{\partial H}{\partial Q} \end{aligned}\right.$$

Using $L = \sqrt{1 + F - G^2} - 1$; $H = \sqrt{1 + P - Q^2} - 1$, introducing the values of $\partial L/\partial F$, $\partial L/\partial G$, $\partial H/\partial P$, $\partial H/\partial Q$ and rearranging

$$\left.\begin{aligned} &(a) \quad R = \frac{F - 2G^2}{L + 1} \\ &(b) \quad S = \frac{G(F + 2)}{L + 1} \\ &(c) \quad -P = \frac{R - GS}{L + 1} \\ &(d) \quad 2Q = \frac{S + RG}{L + 1} \end{aligned}\right| \qquad \left|\begin{aligned} -R &= \frac{P - 2Q^2}{H + 1} \quad (a') \\ S &= \frac{Q(P + 2)}{H + 1} \quad (b') \\ F &= \frac{R + QS}{H + 1} \quad (c') \\ 2G &= \frac{S - RQ}{H + 1} \quad (d') \end{aligned}\right| \quad .. \quad (22)$$

All possible relations that can exist between the invariants can be derived out of the equations (22). We shall deduce a few important ones which will be of use later on.

Substituting (a) and (b) in (d) or (a') and (b') in (d'), we get

$$G = Q \quad .. \quad .. \quad .. \quad (9)$$

Substitution of (a) and (b) in (c') or (a') and (b') in (c) gives

$$(L + 1)(H + 1) = 1 + G^2 \quad .. \quad (18)$$

Comparing (b) and (b')

$$\frac{F + 2}{L + 1} = \frac{P + 2}{H + 1} = \frac{S}{G}$$

$$\therefore \quad \frac{S}{G} = \frac{F - P}{R} = \frac{F + P + 4}{L + H + 2}$$

Comparing (a) and (a')

$$R = \frac{F - 2G^2}{L + 1} = \frac{2Q^2 - P}{H + 1}$$

$$\therefore \quad R = \frac{F - P}{L + H + 2} = \frac{F + P - 4G^2}{R}$$

and we have the relations

$$\frac{S}{G} = \frac{F - P}{R} = L + H + 2 = \sqrt{F + P + 4} \quad .. \quad .. \quad (23)$$

$$R^2 + 4G^2 = \frac{S^2}{G^2} - 4 = F + P \quad .. \quad .. \quad .. \quad (24)$$

Finally we can write (22) (d) and (d') in the form

$$\left.\begin{aligned} \frac{S}{G} + R &= 2(L + 1) \\ \frac{S}{G} - R &= 2(H + 1) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (25)$$

We shall next deduce some relations existing between the several *space invariants* according to Born's theory. Let

$$F_1 = \mathbf{B}^2 + \mathbf{E}^2 ; \; P_1 = \mathbf{D}^2 + \mathbf{H}^2 ; \; M = (\mathbf{D}\,\mathbf{B}) ; \; N = (\mathbf{E}\,\mathbf{H}) ;$$
$$J = (\mathbf{D}\,\mathbf{E}) ; \; K = (\mathbf{B}\,\mathbf{H})$$
$$l_1 = (1 + \mathbf{B}^2) ; \; m_1 = (1 + \mathbf{D}^2) ; \; l_2 = (1 - \mathbf{H}^2) ; \; m_2 = (1 - \mathbf{E}^2)$$
$$R_1 = (\mathbf{B}\,\mathbf{H}) + (\mathbf{D}\,\mathbf{E}) = K + J$$
$$S_1 = (\mathbf{B}\,\mathbf{D}) - (\mathbf{E}\,\mathbf{H}) = M - N$$

The action functions U and V of Born's theory can be written

$$U = \sqrt{l_1 m_1 - M^2} - 1 = \sqrt{1 + \mathbf{B}^2 + \mathbf{D}^2 + \mathbf{S}^2} - 1$$
$$V = \sqrt{l_2 m_2 - N^2} - 1 = \sqrt{1 - \mathbf{E}^2 - \mathbf{H}^2 + \mathbf{S}^2} - 1$$

where

$$\mathbf{S} = (\mathbf{D} \times \mathbf{B}) = (\mathbf{E} \times \mathbf{H})$$ [5]

From the relations[6]

$$\left.\begin{aligned} U + 1 &= M/G \\ V + 1 &= N/G \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (26)$$

we have,

$$U + V + 2 = \frac{M + N}{G} = \frac{S}{G} = L + H + 2 \quad .. \quad .. \quad (27)$$

Observing that $U = L + J$, and $V = L - K$, we have

$$2(U + 1) = 2(L + 1) + 2J = \frac{S}{G} + R + 2J, \quad \text{from (25)}$$

$$= \frac{S}{G} + K - J + 2J = \frac{S}{G} + R_1$$

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[5] Born-Infeld, *Proc. Roy. Soc.*, A, 1935, **150**, 159.

[6] Born-Infeld, *Proc. Roy. Soc.*, A, 1934, **147**, 545, equation (h).

hence the relations

$$\left.\begin{aligned} \frac{S}{G} + R_1 &= 2\ (U + 1) \\ \frac{S}{G} - R_1 &= 2\ (V + 1) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (28)$$

analogous to (25).

Again, $S_1 = M - N = G\ (U - V)$, from (26)

$$= G\ (L + J - I + K)$$

$$\therefore \quad S_1 = GR_1 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (29)$$

The relations between the primary and secondary field vectors in Born's theory when L, H, and U, V are taken as the action functions, *viz.*,

$$\left.\begin{aligned} \mathbf{H} &= \frac{\partial L}{\partial \mathbf{B}};\ \mathbf{D} = -\frac{\partial L}{\partial \mathbf{E}} \\ \mathbf{B} &= \frac{\partial H}{\partial \mathbf{H}};\ \mathbf{E} = \frac{\partial H}{\partial \mathbf{D}} \end{aligned}\right\}$$

and,

$$\left.\begin{aligned} \mathbf{E} &= \frac{\partial U}{\partial \mathbf{D}};\ \mathbf{H} = \frac{\partial U}{\partial \mathbf{B}} \\ \mathbf{D} &= -\frac{\partial V}{\partial \mathbf{E}};\ \mathbf{B} = -\frac{\partial V}{\partial \mathbf{H}} \end{aligned}\right\}$$

can be written in the forms

$$\left.\begin{aligned} \mathbf{H}\ (L + 1) &= \mathbf{B} - G\,\mathbf{E} \\ \mathbf{D}\ (L + 1) &= \mathbf{E} + G\,\mathbf{B} \\ \mathbf{B}\ (H + 1) &= \mathbf{H} + G\,\mathbf{D} \\ \mathbf{E}\ (H + 1) &= \mathbf{D} - G\,\mathbf{H} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (30)^7$$

and,

$$\left.\begin{aligned} \mathbf{E}\ (U + 1) &= l_1\,\mathbf{D} - M\,\mathbf{B} &&= \mathbf{D} + (\mathbf{B} \times \mathbf{S}) \\ \mathbf{H}\ (U + 1) &= m_1\,\mathbf{B} - M\,\mathbf{D} &&= \mathbf{B} - (\mathbf{D} \times \mathbf{S}) \\ \mathbf{D}\ (V + 1) &= l_2\,\mathbf{E} + N\,\mathbf{H} &&= \mathbf{E} - (\mathbf{H} \times \mathbf{S}) \\ \mathbf{B}\ (V + 1) &= m_2\,\mathbf{H} + N\,\mathbf{E} &&= \mathbf{H} + (\mathbf{E} \times \mathbf{S}) \end{aligned}\right\} \quad .. \quad .. \quad (31)$$

Substituting for M and N in (31) from (26) and using (30) we get easily

$$\left.\begin{aligned} l_1 &= (L + 1)\ (U + 1) \\ m_1 &= (H + 1)\ (U + 1) \\ l_2 &= (H + 1)\ (V + 1) \\ m_2 &= (L + 1)\ (V + 1) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (32)$$

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[7] There is a misprint in Born-Infeld, *Proc. Roy. Soc.*, A, 1934, **144**, 438, second formula in (3, 10A) where in the numerator $\mathbf{D} + Q\,\mathbf{H}$ should read $\mathbf{D} - Q\,\mathbf{H}$

Multiplying the equations (31) scalarly by **D**, **B**, **E** and **H** respectively, we have

$$\left.\begin{aligned} J\,(U+1) &= \mathbf{D}^2 + \mathbf{S}^2 \\ K\,(U+1) &= \mathbf{B}^2 + \mathbf{S}^2 \\ J\,(V+1) &= \mathbf{E}^2 - \mathbf{S}^2 \\ K\,(V+1) &= \mathbf{H}^2 - \mathbf{S}^2 \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (33)$$

Similarly multiplying (30) scalarly by **B**, **E**, **H**, **D** respectively

$$\left.\begin{aligned} K\,(L+1) &= \mathbf{B}^2 - G^2 \\ J\,(L+1) &= \mathbf{E}^2 + G^2 \\ K\,(H+1) &= \mathbf{H}^2 + G^2 \\ J\,(H+1) &= \mathbf{D}^2 - G^2 \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (34)$$

From (34) we deduce immediately

$$\left.\begin{aligned} F_1 &= (L+1)\,R_1 \\ P_1 &= (H+1)\,R_1 \\ F_1 - P_1 &= RR_1 \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (35)$$

From (33) and (34), using $U = L + J = H + K$, and $V = L - K = H - J$ we have

$$K\,J = G^2 + \mathbf{S}^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (36)$$

$$\mathbf{S}^2 = (\mathbf{B}^2\,\mathbf{D}^2) - (\mathbf{B}\,\mathbf{D})^2 = \left(\frac{K + G\,M}{H+1}\right)\left(\frac{J + G\,M}{L+1}\right) - M^2$$

$$= \frac{(K + G\,M)\;(J + G\,M)}{1 + G^2} - M^2 \text{ from (18)}$$

$$\therefore\ \mathbf{S}^2 = \frac{K\,J - M\,N}{1 + G^2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (37)$$

From (36), (37) and (26), we easily derive

$$(U+1)\,(V+1) = 1 - \mathbf{S}^2 \quad .. \quad .. \quad .. \quad .. \quad (38)$$

Coming now to vector products of the field quantities, in addition to **S**, the two expressions $(\mathbf{B} \times \mathbf{H})$ and $(\mathbf{E} \times \mathbf{D})$ are equal (see Reference[5]). By suitably multiplying equations (30) and (31) vectorially with the proper field components we get at once

$$(\mathbf{B} \times \mathbf{H}) = (\mathbf{E} \times \mathbf{D}) = G\,\mathbf{S} \quad .. \quad .. \quad .. \quad .. \quad (39)$$

In an entirely analogous manner we can derive from (30),

$$\left.\begin{aligned} (\mathbf{B} \times \mathbf{E}) &= -\,(L+1)\,\mathbf{S} \\ (\mathbf{H} \times \mathbf{D}) &= -\,(H+1)\,\mathbf{S} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (40)$$

4. Invariants of Schrödinger's Representation.

Denoting the invariants of Schrödinger's representation corresponding to F, G, P, Q, R, S, by the small letters f, g, p, q, r, s we can derive relations between them by proceeding with (6, A) and (11, A) just as we did with

equations (21). For this purpose we need only add to equations (15) and (16) the relations obtained by multiplying (6, A) and (11, A) respectively by $\frac{1}{2} q_{kl}^*$ and $\frac{1}{2} r_{kl}$ and summing up. This gives

$$s = 4g\frac{\partial \mathcal{L}}{\partial f} - f\frac{\partial \mathcal{L}}{\partial g} \quad .. \quad .. \quad .. \quad .. \quad ..(15, A)$$

$$s = 4q\frac{\partial \mathcal{L}}{\partial p} - p\frac{\partial \mathcal{L}}{\partial q} \quad .. \quad .. \quad .. \quad .. \quad ..(16, A)$$

It is easily seen that the relations in (15), (16), (15, A), (16, A) can be reduced to the following independent relations

$$\left.\begin{aligned} r = 0\,;\ s = -gq = 4 + \frac{f^2}{g^2}, \\ \frac{f}{g} = \frac{p}{q} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (41)$$

when we substitute the proper values for the partial derivatives of $\mathcal{L}$.

The connection between Schrödinger's and Born's invariants can be written down at once from (1), (10) and (14),

$$\left.\begin{aligned} f &= \mathrm{F} - \mathrm{P} - 2i\mathrm{S} \\ g &= 2\mathrm{G} + i\mathrm{R} \\ p &= \mathrm{P} - \mathrm{F} - 2i\mathrm{S} \\ q &= 2\mathrm{G} + i\mathrm{R} \\ r &= 0 \\ s &= -(\mathrm{F} + \mathrm{P}) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (42)$$

and conversely,

$$\left.\begin{aligned} 4\mathrm{F} &= f - p - 2s \\ 4\mathrm{P} &= p - f - 2s \\ 4\mathrm{G} = 4\mathrm{Q} &= g + q \\ 2\mathrm{R} &= i(q - g) \\ 4\mathrm{S} &= i(f + p) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (43)$$

From (41), $s = 4 + \frac{f^2}{g^2}$ gives

$$-\frac{f^2}{g^2} = \mathrm{F} + \mathrm{P} + 4$$

$$= \frac{\mathrm{S}^2}{\mathrm{G}^2} \text{ from (23)}$$

$$\therefore \quad i\mathcal{L} = i\frac{f}{g} = \frac{\mathrm{S}}{\mathrm{G}} = \mathrm{L} + \mathrm{H} + 2 = \frac{\mathrm{F} - \mathrm{P}}{\mathrm{R}} \quad .. \quad .. \quad (44)^8$$

giving an expression of Schrödinger's Lagrangian in terms of Born's invariants. An alternative derivation of this relation, which is perhaps simpler, is

[8] This relation has also been deduced by Marie A. Baudot, *Comptes Rendus*, 1936, **202**, 909–21 and 1158–59.

obtained by writing

$$f = \mathrm{F} - \mathrm{P} - 2i\,\mathrm{S} = \frac{\mathrm{R\,S}}{\mathrm{G}} - 2i\,\mathrm{S}, \text{ from (23)}$$

$$= -\frac{i\,\mathrm{S}}{\mathrm{G}}(2\,\mathrm{G} + i\,\mathrm{R})$$

$$\therefore \quad \frac{f}{g} = -i\,\frac{\mathrm{S}}{\mathrm{G}} \text{ putting in the value of } g \text{ from (42)}$$

$$i.e., \; i\mathcal{L} = \frac{\mathrm{S}}{\mathrm{G}}.$$

We shall *establish directly the analytical equivalence of the two representations* by showing that the equations (3) are an exact transcription of Born's relations (30) between the primary and secondary field vectors. We have therefore to show directly that

$$\left.\begin{aligned} \mathbf{B} + i\,\mathbf{D} &= -\frac{2}{g}(\mathbf{E} + i\,\mathbf{H}) - \frac{f}{g^2}(\mathbf{B} - i\,\mathbf{D}) \\ \mathbf{E} - i\,\mathbf{H} &= \frac{2}{g}(\mathbf{B} - i\,\mathbf{D}) - \frac{f}{g^2}(\mathbf{E} + i\,\mathbf{H}) \end{aligned}\right\}$$

or, using, $g = 2\mathrm{G} + i\,\mathrm{R}$ and $\frac{f}{g} = -i\frac{\mathrm{S}}{\mathrm{G}}$, that

$$\left.\begin{aligned} -2(\mathbf{E} + i\,\mathbf{H}) + i\,\frac{\mathrm{S}}{\mathrm{G}}(\mathbf{B} - i\,\mathbf{D}) &= (2\,\mathrm{G} + i\,\mathrm{R})(\mathbf{B} + i\,\mathbf{D}) \\ 2(\mathbf{B} - i\,\mathbf{D}) + i\,\frac{\mathrm{S}}{\mathrm{G}}(\mathbf{E} + i\,\mathbf{H}) &= (2\,\mathrm{G} + i\,\mathrm{R})(\mathbf{E} - i\,\mathbf{H}) \end{aligned}\right\}$$

Equating real and imaginary parts, this requires proving that

$$\left.\begin{aligned} \frac{\mathrm{S}}{\mathrm{G}}\mathbf{D} - 2\mathbf{E} &= 2\,\mathrm{G}\,\mathbf{B} - \mathrm{R}\,\mathbf{D} \\ \frac{\mathrm{S}}{\mathrm{G}}\mathbf{B} - 2\mathbf{H} &= \mathrm{R}\,\mathbf{B} + 2\,\mathrm{G}\,\mathbf{D} \end{aligned}\right\}$$

and,

$$\left.\begin{aligned} -\frac{\mathrm{S}}{\mathrm{G}}\mathbf{H} + 2\,\mathbf{B} &= 2\,\mathrm{G}\,\mathbf{E} + \mathrm{R}\,\mathbf{H} \\ \frac{\mathrm{S}}{\mathrm{G}}\mathbf{E} - 2\,\mathbf{D} &= \mathrm{R}\,\mathbf{E} - 2\,\mathrm{G}\,\mathbf{H} \end{aligned}\right\}$$

i.e.,

$$\left.\begin{aligned} \mathbf{D}\left(\frac{\mathrm{S}}{\mathrm{G}} + \mathrm{R}\right) &= 2\left(\mathbf{E} + \mathrm{G}\,\mathbf{B}\right) \\ \mathbf{H}\left(\frac{\mathrm{S}}{\mathrm{G}} + \mathrm{R}\right) &= 2\left(\mathbf{B} - \mathrm{G}\,\mathbf{E}\right) \\ \mathbf{B}\left(\frac{\mathrm{S}}{\mathrm{G}} - \mathrm{R}\right) &= 2\left(\mathbf{H} + \mathrm{Q}\,\mathbf{D}\right) \\ \mathbf{E}\left(\frac{\mathrm{S}}{\mathrm{G}} - \mathrm{R}\right) &= 2\left(\mathbf{D} - \mathrm{Q}\,\mathbf{H}\right) \end{aligned}\right\}$$

and in view of (25) these relations become identical with (30), thus establishing the equivalence.

Coming now to the space invariants of Schrödinger's representation, we shall calculate directly from (1) the several scalar and vector products of the complex field vectors.

$$\mathcal{F}^2 = \mathbf{B}^2 - \mathbf{D}^2 - 2i\,\mathrm{M} = \mathrm{R}\,(\mathrm{U}+1) - 2i\,\mathrm{G}\,(\mathrm{U}+1), \text{ from (33)}$$

and (26)

$$\left.\begin{aligned} i.e.,\ \mathcal{F}^2 &= -i\,(\mathrm{U}+1)\,g \\ \text{Similarly } \mathcal{F}^{*2} &= \ \ i\,(\mathrm{U}+1)\,g \\ \mathcal{G}^2 &= \ \ i\,(\mathrm{V}+1)\,g \\ \mathcal{G}^{*2} &= -i\,(\mathrm{V}+1)\,g \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (45)$$

$$\mathcal{F}^2 + \mathcal{G}^2 = \mathrm{F}_1 - \mathrm{P}_1 - 2i\mathrm{S}_1 = \mathrm{R}\mathrm{R}_1 - 2i\mathrm{G}\mathrm{R}_1, \text{ from (35) and (29)}$$

$$\left.\begin{aligned} i.e.,\ \mathcal{F}^2 + \mathcal{G}^2 &= -i\,\mathrm{R}_1\,g \\ f = \mathcal{F}^2 - \mathcal{G}^2 &= -i\,\frac{\mathrm{S}}{\mathrm{G}}\,g \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (46)$$

Regarding the scalar products of different vectors,

$$\left.\begin{aligned} (\mathcal{F}\,\mathcal{G}) &= 2\,\mathrm{G} + i\,\mathrm{R} = g \\ (\mathcal{F}^*\,\mathcal{G}^*) &= 2\,\mathrm{G} - i\,\mathrm{R} = q \\ (\mathcal{F}\,\mathcal{G}^*) &= -i\,\mathrm{R}_1 \\ (\mathcal{F}^*\,\mathcal{G}) &= i\,\mathrm{R}_1 \\ (\mathcal{F}\,\mathcal{F}^*) &= \mathbf{B}^2 + \mathbf{D}^2 \\ (\mathcal{G}\,\mathcal{G}^*) &= \mathbf{E}^2 + \mathbf{H}^2 \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (47)$$

From (46) and (47) we immediately observe that

$$\mathcal{F}^2 + \mathcal{G}^2 = (\mathcal{F}\,\mathcal{G}^*)\,(\mathcal{F}\,\mathcal{G}) \quad .. \quad .. \quad .. \quad .. \quad (48)$$

Finally, calculating the vector products,

$$\begin{aligned} \mathcal{F} \times \mathcal{G} &= \{(\mathbf{B} \times \mathbf{E}) + (\mathbf{D} \times \mathbf{H})\} + i\,\{(\mathbf{B} \times \mathbf{H}) - (\mathbf{D} \times \mathbf{E})\} \\ &= -\mathrm{R}\,\mathbf{S} + 2i\,\mathrm{G}\,\mathbf{S}, \text{ using (39) and (40)} \\ &= i\,g\,\mathbf{S} \end{aligned}$$

Also,

$$(\mathcal{F} \times \mathcal{G}^*) = (\mathbf{B} \times \mathbf{E}) - (\mathbf{D} \times \mathbf{H}) = -\mathbf{S}\,(\mathrm{L} + \mathrm{H} + 2) = -\frac{\mathrm{S}}{\mathrm{G}}\,\mathbf{S}$$

and $(\mathcal{F} \times \mathcal{F}^*) = -2i\,\mathbf{S}$, and similarly for other vector products. Collecting these together,

$$\left.\begin{aligned} &(\mathcal{F} \times \mathcal{G}) = i\,g\,\mathbf{S}; \quad (\mathcal{F}^* \times \mathcal{G}^*) = -i\,q\,\mathbf{S} \\ &(\mathcal{F} \times \mathcal{G}^*) = -\frac{\mathrm{S}}{\mathrm{G}}\,\mathbf{S}; \ (\mathcal{F}^* \times \mathcal{G}) = -\frac{\mathrm{S}}{\mathrm{G}}\,\mathbf{S} \\ &(\mathcal{F} \times \mathcal{F}^*) = -2i\,\mathbf{S}; \ (\mathcal{G} \times \mathcal{G}^*) = -2i\,\mathbf{S} \end{aligned}\right\} \quad .. \quad (49)$$

From equations (49),

$$(\mathcal{F}^* \times \mathcal{F}) = (\mathcal{G}^* \times \mathcal{G}) = \frac{2}{(\mathcal{F}\mathcal{G})}(\mathcal{F} \times \mathcal{G}) \quad \ldots \quad (50)$$

which is equation (13) of Schrödinger's paper. It might also be noticed that all the vector products in (49) are expressed in terms of **S** which becomes equal to zero when $(\mathcal{F} \times \mathcal{G}) = 0$ and $g \neq 0$, so that all the vector products reduce to zero. This corresponds to the Lorentz-transformation which reduces the Maxwell-tensor to the diagonal and makes all the four composing three vectors parallel.

5. *Alternative Complex Representations.*

No complex combinations of the field vectors other than (1) are possible in view of the form of the Maxwell-Born field equations, *viz.*,

$$\left.\begin{aligned} \text{rot } \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \,;\ \text{rot } \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = 0 \\ \text{div } \mathbf{B} = 0 \,;\ \text{div } \mathbf{D} = 0 \end{aligned}\right\}$$

but corresponding to the representations in Born's theory in which the action function is taken as the displacement energy density U or the field energy density V, we can set up analogous complex representations. Corresponding to the equation

$$\mathrm{U} = \mathrm{L} + (\mathbf{D}\,\mathbf{E})$$

of Born's theory, we introduce here

$$\mathcal{U} = \mathcal{L} + (\mathcal{F}\mathcal{G}^*) = \mathcal{L} - (\mathcal{F}^*\mathcal{G}) \quad \ldots \quad \ldots \quad \ldots \quad (51)$$

or, using (48)

$$\mathcal{U} = \mathcal{L} + \frac{\mathcal{F}^2 + \mathcal{G}^2}{(\mathcal{F}\mathcal{G})} = \frac{2\mathcal{F}^2}{(\mathcal{F}\mathcal{G})} \quad \ldots \quad \ldots \quad \ldots \quad (52)$$

From (52) it is seen that the $\mathcal{U}$ we have introduced is twice the component T_{44} of Schrödinger's energy-impulse tensor. If we now express $\mathcal{U}$ as a function of $\mathcal{F}$, $\mathcal{F}^*$ and treat them as primary field quantities, (51) enables us to find $\mathcal{G}$, $\mathcal{G}^*$ as derivaitves of $\mathcal{U}$ with respect to these. In fact

$$\begin{aligned} d\mathcal{U} &= d\mathcal{L} - \mathcal{F}^*\, d\mathcal{G} - \mathcal{G}\, d\mathcal{F}^* \\ &= \frac{\partial \mathcal{L}}{\partial \mathcal{F}}\, d\mathcal{F} + \frac{\partial \mathcal{L}}{\partial \mathcal{G}}\, d\mathcal{G} - \mathcal{F}^*\, d\mathcal{G} - \mathcal{G}\, d\mathcal{F}^* \\ &= \mathcal{G}^*\, d\mathcal{F} + \mathcal{F}^*\, d\mathcal{G} - \mathcal{F}^*\, d\mathcal{G} - \mathcal{G}\, d\mathcal{F}^* \\ &= \mathcal{G}^*\, d\mathcal{F} - \mathcal{G}\, d\mathcal{F}^* \end{aligned}$$

and hence

$$\left.\begin{aligned} \frac{\partial \mathcal{U}}{\partial \mathcal{F}} &= \mathcal{G}^* \\ \frac{\partial \mathcal{U}}{\partial \mathcal{F}^*} &= -\mathcal{G} \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (53)$$

We shall now express $\mathcal{U}$ as a function of $\mathcal{F}$ and $\mathcal{F}^*$. Multiplying the first equation of (3) scalarly by $\mathcal{F}$, we get

$$\mathcal{F}\mathcal{F}^* = -2 - \frac{\mathcal{F}^2 - \mathcal{G}^2}{(\mathcal{F}\mathcal{G})^2}\mathcal{F}^2$$

$$= -2 - \frac{\mathcal{F}^4}{(\mathcal{F}\mathcal{G})^2} + \frac{\mathcal{F}^2\mathcal{G}^2}{(\mathcal{F}\mathcal{G})^2}$$

$$= -2 - \frac{\mathcal{F}^4}{(\mathcal{F}\mathcal{G})^2} + \frac{(\mathcal{F}\times\mathcal{G})^2 + (\mathcal{F}\mathcal{G})^2}{(\mathcal{F}\mathcal{G})^2}$$

$$= -1 - \left(\frac{\mathcal{F}^2}{\mathcal{F}\mathcal{G}}\right)^2 + \frac{(\mathcal{F}\times\mathcal{G})^2}{(\mathcal{F}\mathcal{G})^2}$$

Using (52) and (50), this can be written as,

$$\mathcal{F}\mathcal{F}^* = -1 - \tfrac{1}{4}\mathcal{U}^2 + \tfrac{1}{4}(\mathcal{F}\times\mathcal{F}^{2*})$$

or,

$$\mathcal{U} = -2i\sqrt{1 + \mathcal{F}\mathcal{F}^* - \tfrac{1}{4}(\mathcal{F}\times\mathcal{F}^*)^2} \quad \ldots\ldots \quad (54)$$

Putting in the values of $(\mathcal{F}\mathcal{F}^*)$ and $(\mathcal{F}\times\mathcal{F}^*)$ from (47) and (49) in the square root on the right-hand side of (54), we get the significant result

$$\mathcal{U} = -2i(\mathrm{U}+1) = -2i\sqrt{1 + \mathbf{B}^2 + \mathbf{D}^2 + \mathbf{S}^2} \quad \ldots \quad (55)$$

We could also have deduced (55) immediately from (52) by substituting in the latter the value of $\mathcal{F}^2$ from (45). Equation (54) or (55) appears to contain the essence of the reason why a complex representation of Born's field theory is possible. Of the four actions I, H, U, V possible in Born's theory we see from (54) and (55) that it is only in the last two cases that we can express the action functions directly as functions of the complex combinations specified by (1). This fact also provides the simplest proof of the equivalence of Born's and Schrödinger's representations. For, with

$$\mathcal{U} = -2i(\mathrm{U}+1)$$

we can directly establish (as we shall do a little farther) that the equations (53) are satisfied. We can now put

$$\mathcal{L} = \mathcal{U} - (\mathcal{F}\mathcal{G}^*) = \mathcal{U} + (\mathcal{F}^*\mathcal{G})$$

and show that equations (3) are satisfied. For the value of $\mathcal{L}$ as a function of $\mathcal{F}$ and $\mathcal{G}$,

$\mathcal{L} = \mathcal{U} - (\mathcal{F}\mathcal{G}^*)$ gives

$$\mathcal{L} = \frac{2\mathcal{F}^2}{(\mathcal{F}\mathcal{G})} - \frac{\mathcal{F}^2 + \mathcal{G}^2}{(\mathcal{F}\mathcal{G})}, \text{ from (52) and (48)}$$

$$\text{or } \mathcal{L} = \frac{\mathcal{F}^2 - \mathcal{G}^2}{(\mathcal{F}\mathcal{G})} \qquad (2)$$

which is Schrödinger's form of the Lagrangian.

Just as equations (3) are a transcription of Born's relations (30), we will show directly that the equations (53) are completely equivalent to (31).

Differentiating (54) with respect to $\mathcal{F}$ and $\mathcal{F}^*$

$$(U+1)\frac{\partial \mathcal{U}}{\partial \mathcal{F}} = -i\left\{\mathcal{F}^* - \tfrac{1}{2}[\mathcal{F}^* \times (\mathcal{F} \times \mathcal{F}^*)]\right\} \quad ..(53, A)$$

$$-(U+1)\frac{\partial \mathcal{U}}{\partial \mathcal{F}^*} = i\left\{\mathcal{F} + \tfrac{1}{2}[\mathcal{F} \times (\mathcal{F} \times \mathcal{F}^*)]\right\} \quad ..(53, B)$$

The right-hand side of (53, A) is equal to

$$\begin{aligned} &-i\{\mathcal{F}^* + i(\mathcal{F}^* \times \mathbf{S})\}, \text{ using (49)} \\ &= -i\{(\mathbf{B} + i\mathbf{D}) + i[(\mathbf{B} + i\mathbf{D}) \times \mathbf{S}]\} \\ &= \{\mathbf{D} + (\mathbf{B} \times \mathbf{S})\} - i\{\mathbf{B} - (\mathbf{D} \times \mathbf{S})\} \\ &= (\mathbf{E} - i\mathbf{H})(U+1), \text{ using Born's relations (31)} \end{aligned}$$

Hence (53, A) reduces to

$$\frac{\partial \mathcal{U}}{\partial \mathcal{F}} = \mathcal{G}^*$$

Again, the right-hand side of (53, B) is equal to

$$\begin{aligned} &i\{\mathcal{F} - i(\mathcal{F} \times \mathbf{S})\} \\ &= i\{(\mathbf{B} - i\mathbf{D}) - i[(\mathbf{B} - i\mathbf{D}) \times \mathbf{S}]\} \\ &= \{\mathbf{D} + (\mathbf{B} \times \mathbf{S})\} + i\{\mathbf{B} - (\mathbf{D} \times \mathbf{S})\} \\ &= (\mathbf{E} + i\mathbf{H})(U+1); \text{ and (53, B) reduces to} \end{aligned}$$

$$-\frac{\partial \mathcal{U}}{\partial \mathcal{F}^*} = \mathcal{G}$$

We can, next, introduce analogously the $\mathcal{V}$-representation by putting

$$\mathcal{V} = -2i\sqrt{1 - \mathcal{G}\mathcal{G}^* - \tfrac{1}{4}(\mathcal{G} \times \mathcal{G}^*)^2} \quad .. \quad ..(54, A)$$

or $$\mathcal{V} = -2i(V+1) = -2i\sqrt{1 - \mathbf{E}^2 - \mathbf{H}^2 + \mathbf{S}^2} \quad ..(55, A)$$

and show that,

$$\left.\begin{aligned} \frac{\partial \mathcal{V}}{\partial \mathcal{G}} &= \mathcal{F}^* \\ \frac{\partial \mathcal{V}}{\partial \mathcal{G}^*} &= -\mathcal{F} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (56)$$

(53) and (56) are the analogues of

$$\left.\begin{aligned} \frac{\partial \mathcal{L}}{\partial \mathcal{F}} &= \mathcal{G}^* \\ \frac{\partial \mathcal{L}}{\partial \mathcal{G}} &= \mathcal{F}^* \end{aligned}\right\} \quad .. \quad .. \quad (3)$$

and,

$$\left.\begin{aligned} \frac{\partial \mathcal{H}}{\partial \mathcal{F}^*} &= \mathcal{G} \\ \frac{\partial \mathcal{H}}{\partial \mathcal{G}} &= \mathcal{F} \end{aligned}\right\} \mathcal{H} = \mathcal{L} \quad ..(3, A)$$

(3) and (3, A) are Lorentz-invariant as is evident from the tensor form of the relations (6) and (11). Just as I have elsewhere[9] deduced the Lorentz-

[9] *Proc. Ind. Acad. Sci.*, A, 1936, **4**, 436.

invariance of the field equations derived from U and V in Born's theory, by using semi-vectors, it is possible to deduce that (53) and (56) are also Lorentz-invariant. It is also easily shown that these relations are invariant against Schrödinger's γ-transformations. For example, if on the right-hand sides of (53, A) and (53, B) we replace $\mathcal{F}$ and $\mathcal{F}^*$ by $e^{i\gamma}\mathcal{F}$ and $e^{-i\gamma}\mathcal{F}^*$ the expressions are multiplied respectively by $e^{-i\gamma}$ and $e^{i\gamma}$, as they should in consonance with (53). Similarly (56) also is invariant against γ-transformations.

Let us now make a transformation to the Lorentz-frame in which all the four composing three vectors are parallel, then from (55) and (55, A)

$$\left.\begin{aligned} \mathcal{U} &= -2i\sqrt{1+\mathbf{B}^2+\mathbf{D}^2} \\ \mathcal{V} &= -2i\sqrt{1-\mathbf{E}^2-\mathbf{H}^2} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (57)$$

and if the corresponding "mixture" field be taken as the standard one, *i.e.*, if we do not use any further γ-transformation to abolish either the electric or magnetic field quantities, we have[10]

$$\mathbf{B}^2 + \mathbf{D}^2 = (1 - \mathcal{A}^2)/\mathcal{A}^2$$

and $\mathbf{E}^2 + \mathbf{H}^2 = 1 - \mathcal{A}^2$, so that

$$\left.\begin{aligned} \mathcal{U} &= -2i/\mathcal{A} \\ \mathcal{V} &= -2i\mathcal{A} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (58)$$

or $$\frac{\mathcal{V}}{\mathcal{U}} = \mathcal{A}^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (59)$$

If $\mathcal{U}$ and $\mathcal{V}$ be interpreted as proportional to the "displacement energy" and "field energy" respectively, this shows that they are in the ratio of $\mathcal{A}^2 : 1$, pointing out again another *dissymmetry between field and displacement.*

Treating the *singular case* of Schrödinger, the equation (52) shows that when $(\mathcal{F}\mathcal{G}) = 0$, we should have

$$\mathcal{F}^2 + \mathcal{G}^2 = 0, \text{ and } \mathcal{F}^2 = 0$$

in order that $\mathcal{U}$ may not become infinite. These equations give

$$\mathcal{G} = \pm i\mathcal{F}, \mathcal{F}^2 = 0$$

and lead, just as in Schrödinger's article, to

$$|\mathbf{B}| = |\mathbf{D}|, \text{ and } \mathbf{B} \perp \mathbf{D}$$

when the case of infinitely weak fields is discarded.

Finally coming to *normal and abnormal fields*, these arise in the present representation from the two values of the square root as can be seen from (57). This equation shows that the sign of $\mathcal{U}$ or $\mathcal{V}$ does not depend upon the fact of either $\mathcal{A} > 0$ or $\mathcal{A} < 0$, but on taking the positive or negative sign of the square root. $\mathcal{U}$ or $\mathcal{V}$ could be positive imaginary or negative imaginary just like $\mathcal{L}$ but here for a different reason.

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[10] See Reference (1); footnote on p. 472.

IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

Part IV. Colloidal Arsenious Sulphide.

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In previous papers we have given the results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric hydroxide,[1] thorium hydroxide,[2] and prussian blue[3] dialysed and diluted to different extents ; in the case of prussian blue cataphoretic speed measurements on ageing and on exposure to sunlight have also been given. In the present paper the results of similar measurements of colloidal arsenious sulphide as well as of changes in its composition under different conditions are presented.

Experimental.

Hydrogen sulphide gas was bubbled through four litres of distilled water till saturation. While the gas was still passing one litre of 15 per cent. solution of arsenious oxide was gradually added, stirring the mixture all the time. Hydrogen sulphide was bubbled through the mixture till it contained no free arsenious acid. The excess of hydrogen sulphide was removed by bubbling hydrogen through the sol. In the end the sol was also filtered a number of times. The colour of the sol so obtained was orange yellow with a peculiar greenish fluorescence. All exposures to light and air were avoided as far as experimental conditions could permit (see Section *E*). Dialysis was carried out in a dark room as before[3] and experiments with each sample were completed in as short a time as possible in order to minimise effect of ageing (see Section *D*).

The cataphoretic speed (cat. speed) was measured as before. An equi-conducting solution of HCl was found to be a satisfactory upper liquid.[4] The difference between the direct and reverse movements of the boundary never exceeded 3 to 4 per cent. In all the tables of results, the cat. speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre $\times 10^5$. The concentration of the electrolytes is expressed in millimoles per litre.

The stability was measured by finding out the amount of electrolyte necessary for instantaneous coagulation. The flocculation values are expressed in millimoles of the electrolyte in total volume, *i.e.*, 30 c.c. in this case.

The composition of the sol was determined by finding out the (i) total amount of arsenic, (ii) total amount of sulphur, and (iii) free arsenious acid. For the estimation of total arsenic and sulphur the method adopted was the one used by Chaudhury and Kundu.[5] For the amount of free arsenious acid, the sol was first coagulated by adding an excess of KCl and the coagulum removed by filtration and washed thoroughly with conductivity water; the amount of free arsenious acid was then estimated iodometrically.[6] The total amount of arsenic and sulphur and the amount of free arsenious acid in terms of arsenic are expressed in all the tables in gm. per litre of the sol.

For ageing experiments the sol was kept in a resistance glass flask wrapped in black paper. Portions of sol were removed after different periods of standing and the various properties were studied after filtering the sol in order to remove precipitates formed as a result of ageing.

For light experiments equal volumes of colloidal arsenious sulphide were kept in resistance glass beakers (of the same capacity) covered with glass plates. A 500 C. P. tungsten filament lamp was used as the source of artificial light; the lamp was kept vertically above the beaker containing the sol. In the case of sunlight experiments the beakers containing the sol were directly exposed.

Results and Discussion.

A. Changes in cataphoretic speed, composition and stability with progress of dialysis.—The results of these experiments are given in Table I.

TABLE I.

Period of dialysis in days	Total As	Free arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	$MgCl_2$
0	2·172	0·0000	2·194	66·52	1·230	0·0202
2	2·156	0·0045	2·145	56·98	1·365	0·0190
5	2·137	0·0135	2·095	32·25	1·605	0·0172
8	2·128	0·0300	2·053	18·23	1·830	0·0156
11	2·090	0·0195	2·040	33·25	1·575	0·0166
14	2·070	0·0120	2·029	38·15	1·425	0·0180
20	2·032	0·0120	2·012	42·75	1·350	0·0187
28	2·013	0·0120	2·002	52·40	1·275	0·0193
31	1·994	0·0120	1·996	10·55	0·825	0·0080

It will be seen from the results that with the progress of dialysis

(1) the amount of arsenic in the sol continuously decreases ;

(2) the amount of free arsenious acid increases upto a period of 8 days after which it decreases till 14 days when it does not change any more during further dialysis ;

(3) the amount of sulphur continuously decreases ;

(4) the cat. speed decreases upto 8 days after which it increases till 28 days when it decreases again ;

(5) the stability with reference to KCl increases upto 8 days and decreases continuously thereafter ;

(6) the stability with reference to $MgCl_2$ decreases upto 8 days after which it increases till 28 days when it decreases again.

The changes in the composition of the sol suggest that a portion of arsenious sulphide hydrolyses during dialysis giving rise to arsenious acid and hydrogen sulphide. A part of the arsenious acid passes out in the dialysate—this accounts for a decrease in the amount of arsenic in the sol (see 1 above). A portion of the hydrogen sulphide escapes as gas and of that which remains in the dissolved condition, a certain amount must also be passing out in the dialysate—these two causes account for a decrease in the amount of sulphur in the sol (see 3 above). Some of the dissolved H_2S may get oxidised giving rise to SO_2 which may react with H_2S producing polythionic acids and sulphur. The sulphur might absorb polythionate ions and pass into colloidal sulphur (*cf.* Freundlich and Nathansohn[7]). The changes in the amount of arsenious acid suggest that upto 8 days the rate of its production by hydrolysis is greater than that of its passing out in the dialysate and that between 8 and 14 days the rate of passing out of arsenious acid in the dialysate is greater than that of its production, while after 14 days both the rates of production of arsenious acid and its passing out in the dialysate are about the same. The rate of hydrolysis is faster in the beginning and slower towards the end possibly because the sol does not contain to start with any free electrolytes and later on complications are introduced due to production of colloidal sulphur as well as changes in the distribution of the preferentially adsorbed ions on the surface of the colloidal particles as a result of introduction of electrolytes in the sol.

The amounts of total arsenic and sulphur in the freshly prepared sol are not according to the formulæ As_2S_3. This is probably due to the fact that during the preparation of the sol a portion of hydrogen sulphide gets oxidised ultimately giving rise to colloidal sulphur as stated above ; the arsenious sulphide sol thus contains some colloidal sulphur also from the

beginning. The composition of colloidal arsenious sulphide prepared in different ways has been represented as $X_2As_2S_3$, $H_2As_2S_4$ by Pauli and Semler,[8] $m.As_2S_3$, H_2S by Linder and Picton[9] and As_2S_3, H_2S by Chaudhury and Kundu[5] (also see Burton and Annetts[10] and Krestinskaya[11]).

The initial cat. speed changes during dialysis in this case (see 4 above) are not similar to those observed with colloidal gold,[12] ferric hydroxide,[1] thorium hydroxide[2] and prussian blue.[3] This is due to the changes in the composition of this sol during dialysis.

The fact that the amount of free arsenious acid in the sol increases upto a dialysis of 8 days and decreases thereafter upto 14 days, while the cat. speed decreases upto 8 days and increases thereafter upto 28 days suggests that the variation in the amount of free arsenious acid upto 14 days might have some bearing on the changes in the cat. speed during that period. In the following table the result of changes in the cat. speed when small increasing amounts of arsenious acid are added to the sols dialysed for different periods are presented.

TABLE II.

Sol. dialysed for 5 days		Sol. dialysed for 25 days		Sol. dialysed for 31 days	
Concentration of arsenious acid	Cat. speed	Concentration of arsenious acid	Cat. speed	Concentration of arsenious acid	Cat. speed
0·000	30·35	0·000	65·10	0·000	47·10
0·025	34·15	0·009	65·35	0·009	43·05
0·125	41·45	0·047	64·60	0·094	42·90
0·250	43·55	0·940	54·70	0·469	41·55
1·250	22·50	9·400	51·50	4·687	40·50
12·500	20·95	46·875	41·20		
170·000	15·75	139·350	35·60		

It will appear from the results that the cat. speed first increases and then decreases in the case of sol dialysed for 5 days. In the case of the sol dialysed for 25 days only a slight rise occurs in the presence of small amounts of arsenious acid, while for sols dialysed for longer periods the cat. speed continuously decreases. S. N. Mukherjee[13] observed that the cat. speed of

arsenious sulphide diminishes on the addition of arsenious acid, while Mukherjee, Raichaudhuri and Rajkumar[14] noticed that the cat. speed of As_2S_3 sol increases in the presence of small amounts of H_3AsO_3 although it decreases when larger amounts of the acid are added to the sol. Our results support both the observations. The difference in the behaviour in different cases is due to a difference in the composition of the sol, the preferential adsorption of the ions being affected to different extents on account of differences in the nature and amounts of electrolytes present in each sol.

From Table II, it will appear that the initial rise of cat. speed increases with a decrease in the period of dialysis. A greater initial rise of cat. speed on addition of small increasing amounts of arsenious acid is therefore likely to occur in the case of the freshly prepared sol containing no free arsenious acid than that of the sol dialysed for 5 days and containing some free arsenious acid from the beginning. The fact that the cat. speed of the freshly prepared sol first increases and then decreases on the addition of small increasing amounts of arsenious acid will incline one to the view that the cat. speed of the sol might have increased immediately after keeping the sol for dialysis and before 2 days, *i.e.*, as soon as traces of arsenious acid were produced as a result of hydrolysis—this might have occurred during the first couple of hours of dialysis and hence not noticed in the experiments described here. Leaving aside this particular point, it is clear that the decrease in the cat. speed upto 8 days is due to an increase in the amount of arsenious acid in the sol. Between 8 and 14 days the cat. speed has increased and this is due to a decrease in the amount of arsenious acid (Table I) during that period. Thus the cat. speed changes upto 14 days' dialysis are primarily due to changes in the amount of arsenious acid in the sol which affect the preferential adsorption of the ions on the surface of the colloidal particles.

The cat. speed changes between 14 and 31 days, *i.e.*, first an increase (between 14 and 28 days) and then a decrease (between 28 and 31 days) can be explained as done by Desai and co-workers[1,2,3] by considering the process of dialysis as a reverse of the case of adding small increasing amounts of the peptising electrolyte to the colloid. In the present case, the sol is probably peptised by sulphide and hydrosulphide ions. Although it has not been possible to take measurements of cat. speed of As_2S_3 sol on adding small increasing amounts of hydrogen sulphide, it is highly probable that, as in the case of other peptising agents and sols, in this case also the cat. speed will first increase and then decrease on adding small increasing amounts of hydrogen sulphide. The amount of total sulphur has continuously decreased between 14 and 31 days as before 14 days. This decrease is due to escape of H_2S as gas and in the dialysate as stated earlier. The amount of the

peptising ions must therefore be continuously decreasing between 14 and 31 days and therefore the cat. speed should first increase and then decrease as stated by Desai and co-workers.[1,2,3] Thus the cat. speed changes between 14 and 31 days of dialysis are primarily due to changes in the amount of the peptising ions in the sol which alter the distribution of the ions on the surface of the particles.

Upto a dialysis of 8 days stability has increased although cat. speed has decreased. This might perhaps be due to replacement of arsenious acid from the surface of the particles by KCl, which process will increase the cat. speed (from a comparison of the results given in Table II with those for KCl given in Section *C*, it will appear that the initial increase in the cat. speed is greater in the presence of KCl than arsenious acid) and hence a larger amount of KCl would be required for coagulation of sols dialysed for relatively long periods than in the beginning when the amount of arsenious acid is relatively small. The stability changes with reference to KCl (Table I) between 8 and 28 days might be primarily due to preferential adsorption of similarly charged ions (Cl-ions) as in the cases of ferric and thorium hydroxide and prussian blue where the stability also decreased in spite of increase of cat. speed. The stability changes between 28 and 31 days are primarily due to changes in cat. speed during that period.

The stability changes with reference to $MgCl_2$ are primarily due to changes in the cat. speed—greater cat. speed greater stability and *vice versa* because the preferential adsorption of the similarly charged ions is probably not allowed to take place in the presence of bivalent coagulating ions.[1,2,3] The productions of slight turbidity on the addition of $MgCl_2$ to the sol containing free arsenious acid does not seem to have any marked influence on the stability of the sol.

B. Changes in cataphoretic speed and stability of arsenious sulphide sol dialysed and diluted to different extents.—Sols of different concentrations were prepared by adding requisite amounts of conductivity water to the original sol. The original sol has dilution 1 ; dilutions of other sols have been obtained from the value of the ratio $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$. The results of these experiments are given in the following table :—

TABLE III.

Period of dialysis in days	Dilution											
	1			1·33	2			4			8		
	Cat. speed	Flocculation values		Cat. speed	Cat. speed	Flocculation values		Cat. speed	Flocculation values		Cat. speed	Flocculation values	
		KCl	$MgCl_2$			KCl	$MgCl_2$		KCl	$MgCl_2$		KCl	$MgCl_2$
0	50·65	1·620	0·016	40·75	33·60	1·89	0·020	21·70	2·40	0·023	17·40	3·15	0·028
4	34·15	1·935	0·012	30·30	24·85	2·52	0·016	17·55	3·37	0·017	14·35	4·26	0·021
8	26·10	2·160	0·010	24·05	20·85	2·84	0·011	15·65	3·96	0·012	13·25	5·25	0·012
17	39·25	1·635	0·016	38·30	36·15	2·40	0·022	33·30	3·06	0·025	33·45	4·02	0·030
23	45·70	1·530	0·020	45·80	46·10	2·02	0·024	48·30	2·58	0·030	54·25	3·30	00·39
29	36·00	1·260	0·014	33·30	28·40	1·62	0·017	31·80	1·95	0·019	43·70	2·34	0·022
31	21·40	0·610	0·007	22·65	24·80	0·81	0·009	29·00	0·93	0·009	41·20	1·05	0·010

It will be seen from the table that on diluting the sol the cat. speed (horizontal rows), (*a*) continuously decreases for sols dialysed for 0, 4 and 8 days, (*b*) first decreases and then shows a tendency of increase for sol dialysed for 17 days, (*c*) continuously decreases for sols dialysed for 23 and 31 days and (*d*) first decreases and then increases for sol dialysed for 29 days ; however in all the cases, the stability with reference to KCl and $MgCl_2$ continuously increases (horizontal rows) on diluting the sol. For all the samples of the sol having different dilutions, the cat. speed during dialysis first decreases and then increases after which it again decreases (vertical columns) (*cf.* Section *A*) ; the results of stability with reference to KCl and $MgCl_2$ (vertical columns) are also exactly similar to those given before in Section *A*.

From the above results, it is quite clear that in the case of arsenious sulphide sol the changes in cat. speed on dilution of sols dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxide and prussian blue.[1,2,3] This is due to the fact that the composition of the sol continuously changes during dialysis which affects distribution of the ions adsorbed on the surface of the colloidal particles as shown in Section *A* ; hydrolysis of arsenious sulphide will also perhaps increase with dilution of the sol, the size of the particles decreasing at the same time. Peculiar changes in cat. speed on dilution of As_2S_3 sol observed by Mukherjee and co-workers[15] are also probably due to a difference in the composition of the various samples tried by them. Mukherjee and Ganguly[16] also observed as

has been done by us that the stability as determined by flocculating values with electrolytes increases on dilution. It may be concluded that the results of stability and cat. speed measurements of colloidal arsenious sulphide should not be utilised either to prove or disprove any of the existing ideas about coagulation of colloids in view of considerable differences that are likely to be produced as a result of changes in the composition of different samples of the sol.

C. Measurements of cat. speed of arsenious sulphide sol (dialysed for different periods) from the point of view of critical potential.—The results of these experiments are given in the following table :—

TABLE IV.

Electrolyte	Period of dialysis	Initial cat. speed	Initial rise in cat. speed	Cat. speed at which sol begins to coagulate	Concentration of electrolyte at which sol begins to coagulate
HCl ..	5 days	28·60	33·80	15·90	25·00
	25 ,,	65·50	24·00	26·90	12·50
	31 ,,	46·80	nil	28·50	17·50
KCl ..	5 ,,	29·20	22·40	25·40	50·00
	25 ,,	63·10	23·75	25·85	37·50
	31 ,,	45·35	nil	29·50	25·00
$MgCl_2$ ..	5 ,,	26·25	nil	12·80	0·25
	25 ,,	63·70	nil	14·15	0·37
	31 ,,	45·35	nil	18·20	0·25
K_2SO_4 ..	5 ,,	17·30	36·20	27·65	25·00
	25 ,,	62·40	14·35	25·00	18·75
$MgSO_4$ ..	5 ,,	15·95	nil	10·40	0·37

It will be seen from the results that the initial rise in the cat. speed when small increasing amounts of electrolytes are added to the sol does not occur in those cases where the electrolyte contains a bivalent coagulating ion.[1,2,3] Further, even in the case of electrolytes with univalent coagulating ions, the initial rise is not noticed with those samples of the sol which are dialysed for long periods. The initial increase in the cat. speed is due to preferential adsorption of the similarly charged ions and this may not be noticed when the coagulating ion is multivalent. The non-observance of initial rise even with the univalent coagulating ions for sols dialysed for longer periods is due to changes in the composition of the sol as stated before.

Mukherjee and co-workers[17] observed that the cat. speed of As_2S_3 sol continuously decreases on adding small increasing amounts of HCl, while Nanitski and Proskurnin[18] got first an increase and then a decrease with HCl. Freundlich and Zeh[19] observed that when KCl is added to As_2S_3 sol the cat. speed continuously decreases, while Kruyt and co-workers[20] got a continuous increase with this electrolyte; Mukherjee and co-workers[21] got with KCl results similar to those of Freundlich and Zeh as well as of Kruyt and co-workers and further observed that in some cases the cat. speed with KCl first decreases and then increases. From what has been stated above it is clear that the differences in the results of different investigators working with the same electrolytes are probably due to differences in the composition of the As_2S_3 sols tried by them.

From the table it will appear that the value of cat. speed at which coagulation takes place lies between 10·40 and 29·50. It would thus appeal that these results as a whole do not support the idea of critical potential.[22] The variation in the value of critical cat. speed for individual electrolytes is, however, generally small. The results show that generally the value of critical cat. speed at which coagulation begins is lower for bivalent coagulating ions than for univalent ones (*cf.* Powis[23] and Chaudhury[24]).

The variation in the value of the critical cat. speed in different cases is due to preferential adsorption of the stabilising ions which is considerably modified by the valency of the coagulating ions as suggested by Desai and co-workers.[1,2,3] In the case of colloidal As_2S_3 the differences are further increased as a result of changes in the composition of the sol—varying amounts of arsenious acid, H_2S and colloidal S.

D. Influence of ageing on the cataphoretic speed, stability and composition of the arsenious sulphide sol.—The precipitates formed as a result of ageing were removed by filtration before studying the various properties. The results of these experiments are given in the following table :—

TABLE V.

Age in days	Total As	Free arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	$MgCl_2$
0	1·306	0·00263	1·426	37·05	1·70	0·0252
15	1·287	0·03300	1·412	34·95	2·02	0·0228
30	1·191	0·04175	1·379	29·35	2·22	0·0189
45	1·110	0·05228	1·341	20·50	1·86	0·0168
60	1·093	0·05689	1·282	18·15	1·66	0·0153
90	1·026	..	1·148	16·30	1·60	0·0147

It will appear from the results that the amount of total As and S continuously decreases on ageing, the amount of free arsenious acid in the sol increasing at the same time. These changes are due to decomposition of the arsenious sulphide sol as stated in Section *A*. The decrease in the total amount of As and S (besides that due to escape of H_2S as gas) is due to removal of the precipitate. Arsenious acid and polythionate ions will have stabilising as well as destabilising effect on both colloidal As_2S_3 and S; the formation of precipitate is due to latter effect.

The decrease in the cat. speed is due to an increase in the amount of arsenious acid with an increase in the age of the sol.

The initial increase in the stability with reference to KCl in spite of a decrease of cat. speed is due to preferential adsorption of the stabilising ions as stated in Section *A*. In the case of $MgCl_2$ the stability has continuously decreased with cat. speed as the preferential adsorption of the similarly charged ions has not been probably allowed to take place as a result of bivalency of the coagulating ion.

E. Effect of artificial light and sunlight on the cat. speed and composition of the arsenious sulphide sol dialysed for different periods.—In these experiments also as in the ageing experiments the precipitate formed on exposing the sol to light was removed by filtration before all measurements were made. Any decrease in volume on exposure was made good by adding conductivity water. The results of these experiments are given in Tables VI, VII and VIII.

TABLE VI.

Artificial Light.

Period of exposure in minutes	Total As	Free Arsenious acid in terms of As	Total S	Cat. speed	Flocculation values	
					KCl	$MgCl_2$
0	1·306	0·0028	1·482	37·05	1·70	0·025
50	1·306	0·0214	1·473	31·05	1·76	0·024
100	1·306	0·0337	1·462	27·20	1·85	0·023
150	1·296	0·0416	1·456	23·60	1·72	0·022
200	1·290	0·0484	1·448	21·85	1·60	0 021
300	1·286	0·0536	1·431	19·50	1·18	0·019
500	1·284	0·0623	1·405	17·00	0·86	0·013
900	1·283	.	1·371	15·38	0·58	0·008

TABLE VII.

Sunlight.

Undialysed Sol.

Period of exposure in minutes	Total As	Free arsenious acid in terms of As	Total S	Cat. speed
0	1·529	0·0000	1·467	50·10
30	1·519	0·0024	1·458	51·25
70	1·514	0·0362	1·450	48·35
150	1·500	0·0569	1·425	43·80
300	1·452	0·0825	1·338	34·05
450	1·422	0·1075	1·326	32·05
1,200	1·403	0·1781	1·312	29·85

TABLE VIII.

Sunlight.

Values in columns 1 *and* 2 *refer to sols dialysed for* 25 *and* 35 *days respectively.*

Period of exposure in minutes	Total As		Free arsenious acid in terms of As		Total S		Cat. speed	
	1	2	1	2	1	2	1	2
0	1·471	1·413	0·0437	0·0437	1·422	1·390	41·40	36·20
60	1·442	1·374	0·1000	0·1812	1·373	1·308	35·20	30·05
300	1·307	1·219	0·2256	0·5563	1·222	1·120	21·45	17·40
600	1·258	1·132	0·2751	0·4625	1·169	1·049	18·85	14·25
1,200	1·210	1·074	0·4282	0·6437	1·100	0·967	17·15	11·45

It will appear that on exposing the sol to light the amount of total As and S decreases while that of free arsenious acid continuously increases. These changes are due to hydrolysis of a part of As_2S_3 into arsenious acid and H_2S. H_2S is photochemically oxidised to SO_2 which further reacts

with H_2S giving rise to polythionic acids and S. The latter adsorbs polythionate ions and passes into colloidal sulphur (Freundlich and Nathansohn[7]).

The cat. speed decreases on exposure as the amount of arsenious acid increases except for the undialysed sol where it first increases slightly and then decreases. As stated before (Section *A*) the cat. speed first increases and then decreases on adding small increasing amounts of arsenious acid in the case of sols dialysed for short periods and the initial increase in the cat. speed of the undialysed sol is due to this effect.

The stability with reference to KCl first increases and then decreases on exposing the sol to artificial light (same changes were also noticed with sunlight) (*cf.* Miss Shila Roy[25]), while that with reference to $MgCl_2$ continuously decreases. The stability changes on exposure to light are thus exactly similar to those observed on ageing (Section *D*) and can be explained in the same manner.

Summary.

The cat. speed of colloidal arsenious sulphide with the progress of dialysis decreases upto 8 days after which it increases till 28 days when it decreases again; the amount of total arsenic and sulphur continuously decreases, while that of free arsenious acid increases at first and then remains constant. The stability with reference to KCl first increases and then decreases, while that with reference to $MgCl_2$ changes exactly as the cat. speed. It is shown that changes in cat. speed are as a result of changes in the composition of the sol with the progress of dialysis which in turn affect to different extents the preferential adsorption of the ions on the surface of the colloidal particles.

The changes in cat. speed on dilution of sols dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxide and prussian blue. The stability with reference to KCl and $MgCl_2$ increases regularly on dilution.

The idea of critical potential is not supported in the case of this sol.

The cat. speed decreases generally on ageing and exposure to light; the amount of total arsenic and sulphur (excluding that in the precipitate) decreases, while that of free arsenious acid increases at the same time. The stability with reference to KCl first increases and then decreases, while that with reference to $MgCl_2$ regularly decreases both during ageing and exposure to light.

It is shown that the results with As_2S_3 sol should not be utilised either to prove or disprove any of the existing ideas about coagulation of colloids because changes in the composition of the sol introduce considerable complications.

In the end it may be mentioned that our cataphoretic speed measurements given in the four papers of this series support the physical point of view (based on the adsorption of the ions of the peptising electrolytes by the colloidal particles)[26] about the origin of charge ; the chemical point of view[27] about the origin of charge which is based on the dissociation of the ionogenic complex is not supported by our results. These points will be discussed in detail in a later publication (Paper to be published in September 1936 number of the *Journal of the Bombay University*).

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RAMAN EFFECT IN DIBASIC ACIDS IN CRYSTALLINE STATE.

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Abstract.

A technique for studying Raman Spectra of crystalline and amorphous solids is described. The results of the study of the first three members of the oxalic acid series are given. Malonic and succinic acids have been tried for the first time. Possible modes of vibration of the molecules corresponding to the observed Raman frequencies are discussed. The characteristic frequencies for the acids in the crystalline state are found to be :—

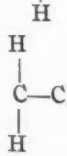
Oxalic acid, 1658, 1590, 1522, 840, 692, 533, 457 cm.$^{-1}$

Malonic acid, 1658, 1471, 1261, 1029, 879, 682, 508 cm.$^{-1}$

Succinic acid, 1654, 1420, 1200, 1153, 927 cm.$^{-1}$

Frequencies 1660 and 1450 cm.$^{-1}$ are ascribed to C = O, and

bindings respectively and those between 1200 and 1000 cm.$^{-1}$ to



while lower frequencies correspond to the vibrations of the two main groups of atoms of the various molecules.

Introduction.

The experimental investigation of Raman effect has been of very great service in explaining the internal structure of various molecules. The characteristic frequencies and the modes of vibration about the various kinds of chemical bonds were the subject of study of workers all over the world for the substances available in the liquid state or large crystals. Menzies[1] for the first time showed that small crystal aggregates, *i.e.*, crystalline, and even amorphous, powders could be used to find the Raman spectrum of these substances. He employed a small flask as the container for the

substance under examination. The light of a quartz mercury-vapour lamp was concentrated on the flask, the scattered radiation being observed in a perpendicular direction. Bär[2] used a rectangular plate-glass cell for holding the crystalline powder and corroborated the results of Menzies. Although the regular reflection from the crystals produced a continuous background which masked all but the strongest modified lines, their discovery showed that single crystals were not essential for studying the molecular scattering. P. Krishnamurti[3] improved the experimental technique by using a triangular cell, two sides of which were silvered and near the third side a quartz mercury lamp was placed. A concentrated solution of didymium chloride was used to absorb the continuous background.

For some time past we have been trying in this laboratory to develop a technique suitable for studying the Raman spectrum in crystal aggregates using the apparatus at our disposal.

Experimental Arrangements.

The substance contained in a hollow plate-glass cube was illuminated on three sides by a specially designed arc of pyrex-glass, as shown diagrammatically in Fig. 1. The arc was generally run at about 3 amperes and could work continuously for very long periods without any attention. With

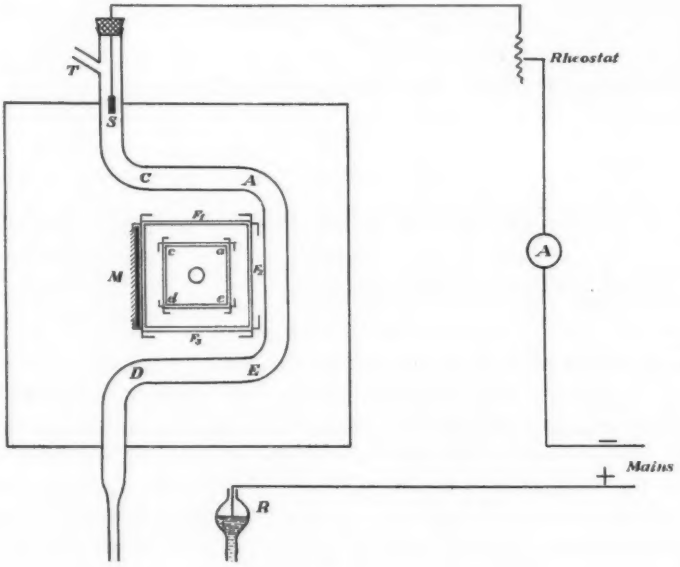


FIG. 1.

this arrangement the intensity of scattered light in case of naphthalene crystals was sufficient for the strongest Raman lines to be observed visually while a few minutes' exposure gave all the modified lines on a plate. The ease in the construction and manipulation of the lamp, its low cost and longer life as compared to the commercial quartz merury lamp are some of the redeeming features of the arrangemet. It is specially suited for substances which require very long exposures.

For holding amorphous substances and fine crystalline powders a slightly different device was used. It consisted of a glass tube of 1·8 cm. bore fitted centrally in the glass cube. Saturated sodium nitrite solution as suggested by Pfund[4] was used as a filter which cuts off effectively the light below λ 4358 Å and in addition absorbed a good deal of the continuous radiation.

The Raman spectra of the first three members of the oxalic acid series (Kahlbaum's and British Drug House Analytic reagents) were photographed in the usual manner using a Carl Leiss Spectrograph of great light-gathering power with a large equilateral prism giving a dispersion of about 70 Å per mm. in the region λ 4358. A Hilger comparator reading upto 1/1000 of a mm. was used for measurement. Backed ortho-special Kodak plates and supersensitive Ilford Iso-zenith plates were used.

Using a set of standard sieves the available chemical was graded into crystals of various sizes. Crystals which passed through 1·5 mm. but not through 1 mm. diameter mesh yielded best results.

Results.

The results of measurements on the different plates are summarised in Tables I, II and III. Table I is for oxalic acid dihydrate and also includes the results of previous workers.

Table II gives the frequencies observed for malonic acid which has been tried for the first time in solid state. The results of Ghosh and Kar on saturated solution of malonic acid in ultra-violet region are given for comparison.

Table III gives the results for succinic acid in the crystalline state which had not been tried before. The exciting line in all cases was $\lambda = 4358 \cdot 3$ Å.

TABLE I.

Oxalic acid dihydrate $\begin{matrix} COOH \\ COOH \end{matrix} 2H_2O$

No.	Wave-length of Raman line in I.A. λ	Intensity I	Wave number in vacuum ν	Frequency shift $\Delta\nu$	$\Delta\nu$ as observed by other authors			
					Krishnamurti[5]	Siva Rao[6]	Hibben[7]	Angus and Leckie[8]
1	4447	1*s*	22481	457				
2	4462	1*s*	22405	533		473		495
3	4494	1*s*	22246	692				
4	4524	2*s*	22098	840	855	851	847	854
5	4668	1*s*	21416	1522		1506	1365 1470	1471
6	4683	0*b*	21348	1590				
7	4698	1*s*	21280	1658		1640 ± 20		1661
						1758		1759

TABLE II.

Malonic acid $H_2C\begin{matrix} COOH \\ COOH \end{matrix}$

No.	λ	I	ν	$\Delta\nu$	$\Delta\nu$ as observed by Ghosh and Kar[9] in saturated solution of malonic acid
1	4457	1*s*	22430	508	
2	4492	1*s*	22256	682	
3	4532	1*s*	22059	879	908
4	4563	1*s*	21909	1029	960
5	4602	0*d*	21677	1261	
6	4657	1*s*	21467	1471	
7	4698	1*s*	21280	1658	
					1737
					2935

TABLE III.

Succinic acid $\begin{matrix} H_2C\cdot OOOH \\ H_2C\cdot COOH \end{matrix}$

No.	λ	I	ν	Δν
1	4542	1*s*	22011	927
2	4589	2*s*	21785	1153
3	4599	2*s*	21738	1200
4	4646	1*s*	21518	1420
5	4697	1*s*	21284	1654

$\nu = 22938$ cm.$^{-1}$ Letters *s*, *b* and *d* denote respectively sharp, broad and diffuse lines.

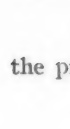
Discussion.

In dibasic acids each molecule consists of two main groups of atoms. The smaller frequencies, namely, 457, 533, 692 and 840 in case of oxalic acid, 508, 682 and 879 for malonic acid and 927 for succinic acid are ascribed to the vibrations of these main groups of their respective molecules.

In oxalic acid the frequency at 840 cm.$^{-1}$ is the strongest and has been observed by all the authors. Corresponding to the frequency 473 cm.$^{-1}$ as found by Siva Rao, and 495 cm.$^{-1}$ as found by Angus and Leckie, the author found two frequencies at 457 and 533 cm.$^{-1}$ Another frequency at 692 cm.$^{-1}$ has also been observed by the author.

In malonic acid, in the crystalline state the frequency observed at 879 cm.$^{-1}$ might correspond to the frequency 908 cm.$^{-1}$ in saturated solution of the acid as reported by Ghosh and Kar.

The larger frequencies are ascribed to the vibrations of the various radicals within each one of the main groups of the various molecules. The frequencies between 1200 and 1000 cm.$^{-1}$ are attributed primarily to the vibrations of the carbon atoms, within these main groups. Morris[10] gives for C—C binding a frequency at 1024 cm.$^{-1}$, while Collins[11] gives two frequencies at 1192 and 1152 cm.$^{-1}$ The results of the dibasic acids also point towards the same conclusion. Oxalic acid does not show any line between 1000 and 1200 cm.$^{-1}$ and its structure shows no $\begin{matrix} H \\ | \\ C\text{—}C \\ | \\ H \end{matrix}$ group. On the other hand,

both malonic and succinic acids show one or two of these frequencies showing the presence of  groups.

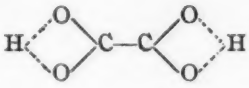
The conclusion of Siva Rao, that the Raman line at about 1450 cm.$^{-1}$ observed in a series of aliphatic compounds is due to the OH group does not appear to be justified, because as is well known, this frequency occurs prominently in the saturated aliphatic hydrocarbons. Available data would tend to show that its origin is to be traced most probably to the δ (C—H) vibration of the CH_2 group. This view is supported by the fact that this frequency is absent in oxalic acid whose structure shows no CH_2 group while it is present in the other two acids which are known to contain one or more CH_2 groups.

Frequency 1660 cm.$^{-1}$ is considered to be the characteristic frequency of the carbonyl (C=O) group. It is shown by all compounds containing this group, such as fatty acids, aldehydes, ketones, esters, anhydrides, etc. The corresponding wave-length also appears in the infra-red absorption spectra of compounds containing this group. The fatty acids have a frequency at about 1660 cm.$^{-1}$, their derivatives have, as a rule, slightly higher frequency which may go up to 1798 in acid chlorides. Thus the replacement of a hydrogen atom in the acid by an alkyl or a halogen group tends to increase the frequency of the carbonyl binding.

Siva Rao found two frequencies, at 1650 and 1750 cm.$^{-1}$, in oxalic acid, the intensity of the latter being greater than that of the former. Hibben has not been able to record any one of these frequencies. Angus and Leckie have found both these frequencies and support Rao's result. The present writer has observed the frequency at 1650 cm.$^{-1}$ but failed to observe the higher frequency in any one of the three dibasic acids studied.

The important work of Kohlrausch and Pongratz[12] on dimethyl and diethyl esters of oxalic, malonic and succinic acids definitely points to the presence of only one frequency for both the carbonyl groups. Even in tri- and tetracarboxylic acids no doubling of frequency occurred. In tautomeric forms such a doubling of frequency may be possible and has been observed. But in non-tautomeric compounds like oxalic acid and succinic acid no such doubling is conceivable. This supports the contention of the present author that in dibasic acids the two carboxylic groups are similarly situated giving rise to only one characteristic Raman frequency.

Recently J. Gupta[13] has proposed for oxalic acid in anhydrous state the structure



while retaining for solution the normal structure —C(OH)=O. B. C. Ray and P. B. Sarkar[14] have proposed a $\left(:C\begin{matrix}O\\OH\end{matrix}\right)^-$ structure for the formate ion in solution retaining the normal structure —C(=O)OH for the acid and its ester in the crystalline state. Small and Wolfenden[15] have opposed such a hypothesis. So far as the present work goes, it shows that there is only one frequency corresponding to carbonyl groups indicating normal structure for both the COOH groups in oxalyic, malonic and succinic acids in the crystalline state.

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